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XXIX CYCLE

Ph.D. Thesis

Advanced geochemical survey and environmental multiscalar risk assessment methodologies applied on topsoils of Campania region (Italy) and in selected areas with high anthropic impact

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Abstract

Environmental quality is fundamental for the well being of human life. Environmental risk assessment and analysis have a crucial role for guaranteeing the safety of the population, especially in intensive urbanized and industrialized areas, such as the Campania region (Italy). In Italy, after the Legislative Decree 152/2006, the environmental risk assessment has become mandatory for contaminated lands such as brownfields and dismantled industrial activities. Despite the importance and fragility of the soil, it is rarely taken into account as a resource to be preserved. Moreover, due to the heterogeneity of many variables involved in the process, the environmental and human health risk assessments are used at the scale of a site, while the regional evaluation is very difficult, and keeps the administration sceptical in taking it into account for land planning and decision-making processes.

During the last years, some international methodologies for ecological and human health risk assessment have been developed by national environmental agencies in many industrialized countries. An idea recently took place regarding the protection of soils: the monitoring of soil should be limited only to risk areas, as opposed to monitoring systems covering the entire territory. Focusing monitoring in selected areas would help to define priorities, increase efficiency of monitoring activities and reduce the monitoring costs. This is the reason why many methodologies for preliminary and simplified risk assessment of (potentially) contaminated sites, for the prioritization and planning of soil remediation and protection programmes, were developed.

The only lack that these methodologies have is the absence of the spatial analysis. The aim of this research was to implement the human health risk assessment. For the purposes of the study we used 3535 topsoil samples, collected across the whole regional territory. The concentrations of 53 elements have been determined at Bureau Veritas Analytical Lab. Ltd (Vancouver, Canada), by means of an Aqua Regia extraction followed by a combination of ICP-MS and ICP-AES methods. After the statistical and cartographic elaboration of these regional dataset, we integrated one of the model of relative risk assessment for single contaminated sites with spatial analysis procedures. In order to support the spatial assessment of contaminated sites at the regional scale, the most suitable tool is the Geographic Information System (GIS). A new approach was applied, in order to assess/rank environmental risk by using geospatial analysis in a GIS platform to adapt a European-wide accepted methodology for the preliminary assessment of human health risks at single contaminated sites to a regional scale. The developed regional risk assessment methodology can be used by the regional administrations to select at regional level the "problem or priority areas". The identification of the problem areas is necessary for developing an efficient monitoring system and to produce a ranking of the risky areas to be used as a reference in determining the development of intervention plans, for better addressing the resources dedicated to the environmental remediation of widely contaminated regions.

The methodology chosen as a reference for the risk assessment procedures is the PRA.MS (Preliminary risk assessment model for the identification of problem areas for soil contamination in Europe, 2005). Following the PRA.MS guidelines, a conceptual model for the human health risk assessment for the Campania region has been based on four different exposure routes: 1) dispersion of contaminants in groundwater, 2) dispersion in surface water, 3) dispersion in air, 4) direct contact with the contaminated media (soils). The source, the pathway and the receptor for each of the exposure route are scored on the base of a quantitative or qualitative analysis of some featuring characteristics (parameters).

A total of 14 representative parameters were chosen, basing on the available regional data for Campania. Starting from these parameters values, the information is aggregated to higher levels in several steps, adopting a mixed additive and multiplicative algorithm, up to the overall risk score. The final risk map is classified according four classes of risk.

This map was useful to identify the problem areas, characterized by a higher risk, where more detailed analysis had to be carried out. The identified area was located in a wide territory in the center of Campania region, between Avellino and Salerno municipalities, an high populated zone, where intensive agricultural and industrial activities are well developed. A high density survey has been carried out in this priority area; the concentrations of 53 elements have been measured on 102 new topsoil samples, followed by statistic and cartographic elaboration of the 15 potentially toxic elements (Sb, As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Sn, Tl, V, Zn) for which the Italian legislation (D.Lgs. 152/06) established the trigger and action limits, by defining the contamination threshold values (CSC) for the amount of metals in topsoils or waters. The new methodology of GIS-based human health risk assessment has been again applied, in order to select sites of particular significance in terms of danger for the resident population. Some small areas characterized by high risk have been identified. New in situ measurements and classic follow up risk assessment should be here carried out to confirm if remediation actions are needed to guaranteeing the safety of the population.

Other works has been contemporaneously elaborated during the PhD. Six months have been spent at the Geological Survey of Finland (GTK), where a work on a humus samples dataset have been carried out, under the supervision of Dr. Timo Tarvainen. Moreover a new Geochemical Atlas will be completed based on inorganic elements and organic compounds concentrations in marine sediments samples, collected in the Gulfs of Naples and Salerno.

Introduction

Soil is a complex mixture of mineral nutrients, organic matter, water, air, and living organisms and its function is to sustain biological productivity, maintain environmental quality, and support human health and habitations (Kalu, 2015). Soil evolution is influenced not only by natural agents, such as morphology and climate, but also by anthropic activities related to both industry and agriculture. Being a boundary between rocks, sediments and ground-water on one side, and vegetation, air, rain, surface water, fauna and human beings on the other, it is an essential factor, acting as regulator of ground-water quality, for filtering harmful chemical elements, for biological and social activities, for agriculture and forestry productions, and at the same time the soil is subject to the effect of pollutants and waste production (Costabile et al., 2004). Pollution of soil is caused mainly by atmospheric fallout from various sources, the most important being industrial and traffic emissions, but other main sources of emissions of potentially hazardous elements are the waste producing areas (including hospital/ industrial/household/municipal solid and liquid wastes, etc., BouKheir et al., 2014). Three million are the estimated potentially contaminated sites in the whole European Union, of which about 250,000 are actually contaminated and in need of remediation (EEA, 2007). Once the soil is degraded, it does not easily reach a new equilibrium. Hosting the deep portions of vegetation, fauna and micro-organisms, where occurs the matter and energy cycles, the soil can be considered as the "live skin" of the hearth and, just as a living being, it has the capability of resistance and adaptability, but, once a certain threshold is reached, it loses most of its function, becoming the dead skin of the hearth (Costabile et al., 2004). Due to the non-biodegradability of potentially hazardous elements, they can easily accumulate in the soil and enter in the food chain, having a significant effect on human health in the long term (BouKheir et al., 2014). Despite its importance and fragility, and the attempt to safeguard it as a significant resource by Thematic Strategy on Soil (Van Camp et al., 2004), it is still not considered by many people as a resource to be preserved.

The men itself is the most dangerous creature for the planet where we live. The uncontrolled activities carried out for decades only for guaranteeing the wellness of some part of population, has lead to an unsustainable situation. The contamination of the environment has finally become an argument of interest for the political institution in the industrialized countries only from the '90s. The need to understand the behaviour of the chemical elements and their compounds in nature has grown with the urgency of environmental and ecological problems (Koljonen, 1992).

To the scientists is asked to find a compromise between the economic and social development of the territory and the safeguard of the environment. Where the ecosystem has already been destroyed, they are involved in the remediation of the territory, trying to minimize, as much as possible, the damage created by the man itself. The knowledge about

the chemical characteristics of contaminants, their chemical reactivity and their capacity of bioaccumulate in the living organisms, is fundamental. Studies about the geological and geochemical compositions of the territory and their variations caused by pollution, the elaboration of those kind of data, the realization of thematic maps showing the spatial distribution of the soil characteristics and their divulgation, are necessary for aiming to a different conception of industrial and, in general, anthropic activities, that take into account the serious consequences for human and environment.

People must understand that where a waste is disposed, agricultural activities can't be carried out. A waste disposal, an industrial activity or an urban expansion cannot be placed everywhere, because each part of territory has a different vulnerability to pollution. Some recent studies proved that some pathologies in the living organisms are more diffused in some particular geographical areas (Albanese et al., 2008a; 2013; Giaccio et al., 2012; Valera et al., 2014). Both land use planning and the developing of "geomedicine" can be helped by the elaboration of regional maps. This is the aim of this doctoral research, where a new methodology, that take in consideration all the elements that are known to be potentially hazardous for the human health, and all the environments where the pollution could spread into, such as surface and ground water, atmosphere, presence of agriculture or urban fabric, has been developed. The methodology has been first applied on a regional area, being an instrument for selecting the main potentially hazardous areas from wide territories, where focusing the attention.

Aim and structure of the thesis

The aim of the research was to implement the environmental risk assessment procedure, in a prospective mostly oriented to the safety of human health, taking into account the actual population and environment exposures, besides the distribution and degree of contamination. The multiscalar approach allowed a passage from regional to local scale. Because of the difficulty in the estimation of many parameters involved in the environmental risk evaluation, regional approaches are not widely diffused in the scientific literature. We tried to develop a new procedure to assess/rank environmental risk, by using geospatial analysis in a GIS platform to adapt a European-wide accepted methodology for the preliminary assessment of human health risks at single contaminated sites to a regional scale. We thought about the new methodology as a quick and easy tool that can be used by the administrations for a better management of environmental risk at regional scale, without wasting resources, and minimizing costs.

The thesis has been structured in chapters following the work phases; moreover, to each chapter corresponds a publication or a work actually in progress:

- The concentrations of 53 elements in 3535 top soil samples of Campania region were

already available from previous surveys carried out by the University of Naples during 2013-2014. The knowledge and analysis of available top soil dataset covering the entire Campania region was necessary as a base for the following regional risk assessment. In Chapter 1, a summary of the statistic and cartographic elaboration of the regional database, is exposed. The whole description can be found in the Environmental geochemical Atlas of Campania soils (De Vivo et al., 2016).

- The second part of the thesis consisted in the elaboration of the new regional risk assessment methodology, which has been described in Chapter 2 and published as a work on a Special Issue of Journal of Geochemical Exploration (Minolfi et al., 2016). Thanks to the new procedure applied on the top soils of Campania region, it was possible to select a priority, potentially hazardous, area, located in the area between Avellino and Salerno municipalities, where a detailed sampling has been carried out.
- The third part of the thesis has been the geochemical survey and the application of the risk assessment methodology in the selected area. The sampling activity, the analytical results, the statistic and cartographic elaboration, and the risk analysis are described in Chapter 3 and will be part of a new publication (Minolfi et al., in progress). The risk analysis applied on selected areas, made possible to find areas where classic follow up risk assessments should confirm if actions, such as plans of rehabilitation or reclamations, should be taken.

Other works has been contemporaneously carried out during the PhD:

- Part of the PhD took place at the Geological Survey of Finland (GTK). Here a work on a humus samples dataset have been carried out, under the supervision of Dr. Timo Tarvainen. The results (Minolfi et al., in press) can be found in Chapter 4.
- In Chapter 5, other works are briefly described. Another small area was chosen for a high density sampling, and is here described. Moreover a new Geochemical Atlas will be completed based on inorganic elements and organic compounds (PAHs and OCPs) concentrations in marine sediments samples, collected in the Gulfs of Naples and Salerno (Minolfi et al., in progress).

List of original publications

I. De Vivo, B., Lima, A., Albanese, S., Cicchella, D., Rezza, C., Civitillo, D., Minolfi, G., Zuzolo, D., 2016. Atlante geochimico-ambientale dei suoli della Campania / Environmental geochemical Atlas of Campania soils. Aracne Editrice, Roma. ISBN 978-88-548-9744-1, pp. 364.

II. Minolfi, G., Albanese, A., Lima, A., Tarvainen, T., Fortelli, A., De Vivo, B., 2017. A regional approach to the environmental risk assessment - Human health risk assessment case study in the Campania region, J. Geochem. Explor. http://dx.doi.org/10.1016/j.gexplo.2016.12.010

III. Minolfi et al., Geochemical follow-up survey in Avellino-Salerno-Sarno river basin-Picentini Mts. area. In progress

IV. Minolfi, G., Jarva, J., Tarvainen, T., Humus samples as an indicator of long-term anthropogenic input – a case study from southern Finland, , J. Geochem. Explor, in press.

V. Minolfi, G., Jarva, J., Tarvainen, T., 2015. Comparison on humus and topsoil geochemical baselines in Southern Finland. Geological Survey of Finland report, pp. 24. http://tupa.gtk.fi/raportti/arkisto/85_2015.pdf

VI. Minolfi, G., Zuluaga, C., Wang, M., Albanese, S., Lima, A., De Vivo B. Atlante dei sedimenti marini dei Golfi di Napoli e Salerno. Aracne Editrice, Roma. In progress

Chapter 1 – Environmental Geochemical Atlas of Campania soil

De Vivo, B., Lima, A., Albanese, S., Cicchella, D., Rezza, C., Civitillo, D., Minolfi, G., Zuzolo, D., 2016. *Atlante geochimico-ambientale dei suoli della Campania / Environmental geochemical Atlas of Campania soils.* Aracne Editrice, Roma. ISBN 978-88-548-9744-1, pp. 364.

1.1 Introduction

1.1.1 Geochemical mapping - State of the art

The mapping of geochemical data is a valid instrument to identify the areas with anomalous contents of potentially toxic elements for human beings and environment. The graphic representation is fundamental for a correct elaboration of these kind of data. Thanks to the knowledge of the chemical composition of the areas where we live, and to the possibility of obtaining a visual representation, it is possible to control the levels of the environmental pollution, to gain an enhanced understating of its effects on humans and animals. This acquired knowledge would allow us to be capable of handling the problems related to the use of territory, varying from agriculture, to forestry, water supplying, waste disposal, industrial pollution, epidemiological studies on the health of humans and animals, use of land. Geochemical mapping can in general lead to a better management of territory, that would potentially result in a greater productivity of the territory itself (Darnley et al., 1995; Plant et al., 2001). Moreover, it is also possible to evaluate the environmental situation, comparing the data measured at distance of years.

In Europe and overbroad several geochemical atlases have been produced by the Geological Surveys (BGS, 1987, 1996, 1997; Plant et al., 1997; Reimann et al., 1998; Bodiš e Rapant, 1999; Kadunas et al., 1999; Ottesen et al., 2000). One of the first project, that started with the collaboration of the National Geological Surveys of 25 European countries, is the FOREGS (*Forum of European Geological Surveys*). A group of researchers from University of Naples "Federico II", University of Sannio and Siena collaborated for representing Italy in this contest, contributing to the realization of the Geochemical Atlas of Europe (Salminen et al. 1998; 2005; De Vos et al., 2006). Several works have been published for the interpretation of the data (Lima et al., 2008, Fedele et al., 2008b). The Italian researches continued the activities during the *EuroGeoSurveys Geochemistry Expert Group* between 2007 and 2011. After 2011 they participated to *GEMAS* and *URGE Project Teams*. In this contest were realized:

- The European Atlas of mineral waters (Reimann and Birke eds., 2010); a special Issue of *Journal of Geochemical Exploration* (Birke et al., 2010), collecting several

scientific contributions on mineral waters (Cicchella et al., 2010a; Dinelli et al., 2010; 2012a; 2012b; Lima et al., 2010);

- The European Atlas of Agricultural soils (Reiman et al., 2014a; 2014b) and several publications about the GEMAS database on agricultural and grazing soils of 25 european countries (Reiman et al., 2008, 2009, 2011; Cicchella et al., 2013, 2014a, Albanese et al., 2015);
- Geochemical Atlas of Europe (De Vivo et al., 2008a; 2008b) based on the FOREGS database, including geochemical data measured on bottom and top soils, river sediments, alluvial sediments and river waters.

1.1.2 Geochemical mapping in Campania region

Campania is the most geochemically investigated region in Italy. The following papers have been already published:

- Campania region's River sediments' Geochemical Atlas (De Vivo et al., 2003 and 2006a) and several scientific publications (Albanese 2007a; Cicchella et al., 2008a; Lima et al., 2003, 2005);
- The Atlas of Urban soils of Naples and province (De Vivo et al. 2006c) and several scientific publications (Cicchella, 2002; Cicchella et al., 2003; 2005; 2008b);
- Urban areas of Avellino, Benevento, Caserta, Ischia Island and Salerno's Geochemical Atlas and several scientific publications (De Vivo et al., 2006c; Lima et al., 2007; Albanese et al., 2007b; 2008 e 2011; Frattini et al., 2006a; 2006b; Fedele et al., 2008; Cicchella et al., 2008c; 2010b);
- Litorale Domizio-Flegreo e Agro Aversano S.I.N. (National Site of Interest) Geochemical Atlas (Lima et al, 2012) and several scientific publications including isotpical studies on environmental media (Bove et al., 2011; Grezzi et al., 2011);
- Other scientific works have been carried out in specific areas with high anthropic impact, such as Sannio river basin (Albanese et al., 2012; Cicchella et al., 2014b). In the same areas there are works about the bioavaiability and transfer of contaminants from agricultural soils to plants (Adamo et al., 2014);
- In areas of Campania Plain contamination of both potentially toxic metals and organic compounds, such as PAH, have been evaluated together with a preliminary human health risk assessment (Albanese et al., 2014).
- Out of campania region have been carried out geochemical surveys by the research group of Napoli University, in Basilicata (Lima et al., 2016), in Monti Peloritani (Lima et al, 2016), in Calabria (De Vivo et al., 1998a) and Sardinia (De Vivo et al., 1997; 1998b; 2001a)

The Geochemical Atlas, published in 2016 and here presented being part of the doctoral work, illustrates the results of several surveys made on top soils of Campania region. Here, on a 13595 km^2 surface, 3535 top soil samples have been collected with a sample density of 1 sample/4 km^2 and analyzed with a combination of ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) in order to measure the concentration of 53 inorganic elements. Several students, working on their Bachelor and Master Thesis at the University of Naples "Federico II", collaborated during the surveys. The organization of the database and the statistical and cartographical elaboration are, instead, part of this PhD work. Only these last part of the work will be discussed in this chapter, together with the description of the 15 potentially toxic elements cartography. For the description of the remaining elements, it is possible to read the Environmental Geochemical Atlas of Campania soils (De Vivo et al., 2016).

1.2 Campania region

Campania region is situated in south Italy (Fig.1.1), and it lies between the Tyrrhenian Sea to the West and the Apennine mountain chain to the East. The whole territory covers an area of about 13,660 km^2. Five are the provinces of the region: Napoli, Salerno, Caserta, Avellino and Benevento, in order of population density (Fig.1.1). The region is the most populated in Italy with a population density of 429 inhabitants/km^2, and the third for the number of inhabitants (ISTAT, 2015), with more than 50% concentrated in the Naples metropolitan area (Albanese et al., 2007). Some inner mountainous areas (Mt. Matese, Cilento area, etc.) are characterized by the presence of small cities with a very low population density, traditionally dedicated to agricultural and pastoral activities.

Fig. 1.1: *Campania region, location in Italy and subdivision in provinces and municipalities.*

1.2.1. Geological and geomorphological settings

The geology of Campania region is the result of different processes. It can generally be distinguished in the eastern hilly/mountainous area and the western coastal low lying area, occupied by alluvial plains. The eastern area is made up of the southern Apennine mountain chain, oriented NE-SW, resulting both from compressive tectonic events, related to the subduction followed by the roll-back of the Adria plate, and from the extensional tectonics related to the opening, since the late Miocene, of the Tyrrhenian sea (Bonardi et al., 2009). Due to the extensional forces, the western area of Campania is occupied by a large subsiding graben (from Pliocene-Pleistocene up to 5 km, Ippolito et al., 1973), filled by sediments originated from the erosion of the Apennine ridge and from products of intensive volcanic activity. The whole area of the graben presently constitutes the Campanian and Sele plains. The volcanism in the Campanian plain is part of the Roman Co-magmatic Province (Washington, 1906), getting younger from Tuscany to Campania. The conditions were ideal for triggering fissure volcanic activities (Peccerillo et al., 2005 and references therein), with different ignimbrite eruptions (Campania Ignimbrites), as well as volcanic complex formations (Roccamonfina, in the north-western sector of the region; Campi Flegrei and Ischia, along the western border of the region; Mt Somma-Vesuvio) (De Vivo, 2006b and references therein; De Vivo et al., 2001b; De Vivo et al., 2010; Rolandi et al., 2003 and ref. therein; Milia and Torrente, 2000; Torrente and Milia, 2013). The volcanic rocks (lava and pyroclastics), dated from about 600 ka to present, are represented by potassic/ultrapotassic rocks (De Vivo et al., 2001b; Rolandi et al., 2003), with alkaline magmatism, characterised by high K_2O content (De Vivo et al., 2010; Peccerillo, 2005). The main sedimentary lithologies consist of: i) limestone, dolostone, siliceous schist and terrigenous sediments (clays, siltstone, sandstone, conglomerate), part of the Mesozoic Units, that characterize mostly the external Apennine domains, ii) the Neogene Units, made up mostly of silico-clastic, carbonatic and evaporitic sediments, and iii) Quaternary sediments represented by alluvial, lacustrine and evaporitic sediments and by pyroclastic fall and flow deposits, occurring mainly in the Campania plain.

1.2.2. Climate and hydrogeology

Campania region has a Mediterranean climate, characterized by hot dry summers and moderate cool rainy winters (Ducci and Tranfaglia 2005). The differences in climate between the high mountains in the interior and the coastal areas are quite large. The maximum temperature during the winter times (January) varies between 11-13°C along the coast, and 5-8°C on the mountainous interior zones, and between 28-31°C/25-28°C during summer; the minimum temperature rarely is below 5-6°C along the coast, while in the inland can be very low during severe winters.

The rainfall regime in Campania has a maximum in autumn/winter, mainly influenced by mountain chains, in terms elevation, location of ridges (barrier effect) and proximity to Tyrrhenian Sea (Ducci and Tranfaglia, 2005). The maximum mean annual rainfall (>1100 mm/yr) occurs in the central part of the Apennine ridge, especially in the Partenio and Picentini Regional Parks, and in the southern Cilento area (up to 1800-2000 mm/yr). The lowest precipitation (600-700 mm/yr) occurs along the coastal plains and in the northeastern part, on the other side of the Appenninc watershed, with the Benevento province (Ducci and Tranfaglia, 2005; Mazzarella and Fortelli, 2012, Fig. 1.2).

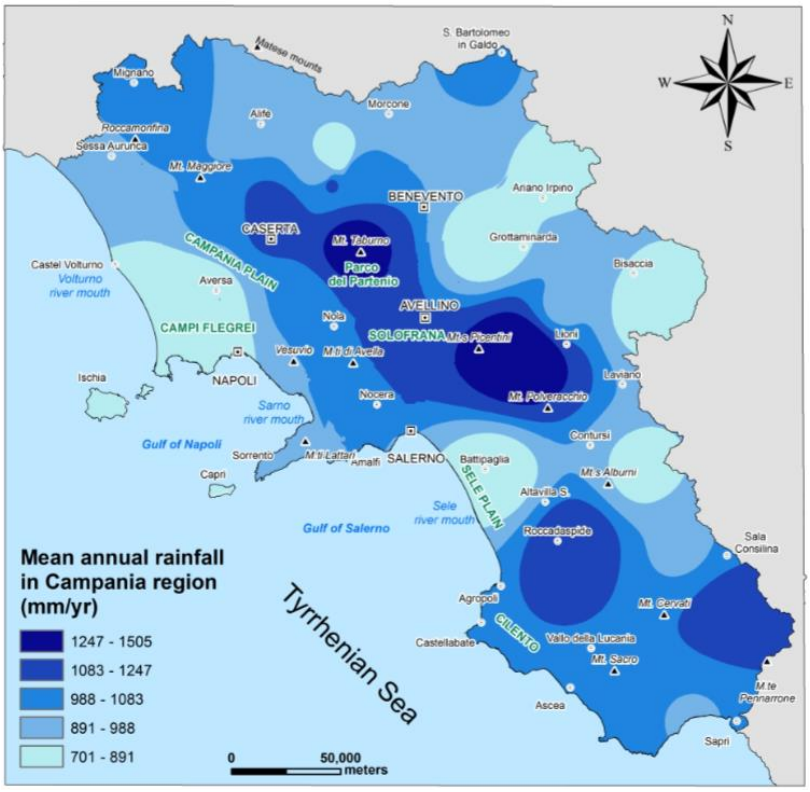


Fig. 1.2: *Mean annual rainfall in Campania region (data from Regional Agrometeorological Network 1999-2012)* .

The hydrography of Campania region is quite simple with two main rivers: Volturno River is 170 km long, with a hydrographic basin covering 5600 km^2, about 40% of the regional territory, located in the northern part of the region; the second river is the Sele, 65 km long and extending over an area of 3200 km^2 in the southern part of the region.

1.2.3. Economy

The economy of Campania has dramatically changed since the 90s, with the development of services and tourism, and the dismantling of the traditional industrial/productive activities, such as mechanical or textile industries. Commercial activities have a 35% share of the economy, services 25%, constructions 10%; industries and restaurants/accommodations have an equal share at 9%, followed by transport and

warehousing (7%), health care centers and assistance (5%), other services (4%) and instruction (1%) (Banca d'Italia, 2015).

As it can be observed from the Land Use map (Fig.3), agriculture is the most intensive activity in the Campania region. In the North, the agricultural activities cover more than 50% of the available land, while in the South farming is mostly developed along the coast, due to the occurrence of mountainous areas. The pyroclastic deposits, covering most of the carbonates and flood-plain deposits located along the coast, help the productivity of this territory. Despite this natural fertility of the volcanic soil, rich in "mineral nutrients", Campania is one of the Italian regions with the highest consumption of fertilizers, containing Cd, Cu and V as pollutants.

After Sardinia and Calabria Regions, Campania is the Southern region with the largest forest area and with the highest percentage (30%) of land covered with national and regional parks and nature reserves (Lombardo et al., 2011).

Fig. 1.3*: Land use map (data from Corine Land Cover 2012).*

Industries are mostly distributed in the northern half of the regional territory. The main industrial activities are connected to vegetable canning, textile, clothes and tannery production. Industrial related pollution can be ascribed to lack of maintenance of the purification and waste-water systems that can lead to an intense pollution of stream water, ground-water and sediment.

No economic mineral deposits occur in Campania; only a few minor bauxite mineral occurrences–of no economic relevance – are located in the Mesozoic rocks of Mt. Matese in the Apennine Mountains (Albanese et al., 2007).

1.3 Sampling sites

During several surveys in Campania region, 3535 surface (top soil) samples were collected over an area of 13595 km^2, with a nominal density of 1 sample/4 km^2 (Fig. 1.4). The real density is different in some areas (Neapolitan Province, urban areas of Salerno, Caserta, Avellino and Benevento and Domizio-Aversano S.I.N. area) because some of these were subjects of specific Geochemical Atlas, for which the sampling density was higher.

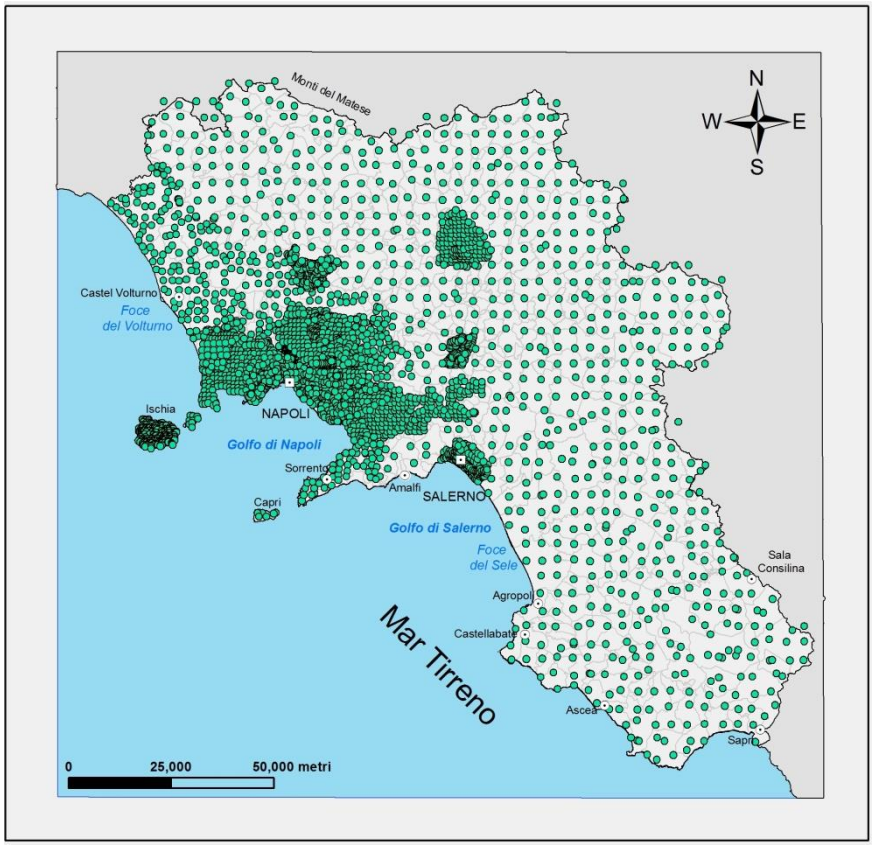


Fig. 1.4:*Geochemical Atlas of Campania region sampling sites .*

The sampling procedures followed the international guidelines established by the FOREGS Geochemistry Group (Salminen et al., 1998): about 1.5 kg soil was collected from a depth between 5 and 15 cm under the ground surface after the removal of the vegetation cover. For each sample field notes were recorded, namely the alphanumerical code, the spatial coordinates of the sampling site and any other useful information about the sampling site, such as local geology, topography, type of soil and vegetation, land use and indication of possibly contaminating anthropogenic activities (roads, industries, use of pesticides,

insecticides etc.). Duplicate samples were collected every 20 sampling sites, on the opposite side of the same cell, in order to estimate the sampling variability.

The database has been organized in such a way that each sample can be uniquely identified by the identification code (ID) and their geographical coordinates (UTM-ED50). The corresponding analytical values have been associated to each ID, together with every possible useful information.

1.4 Analysis and quality controls

The samples were dried under infra-red lamps at a temperature below 35°C, and then disaggregated in a ceramic mortar and sieved through a 2 mm nylon mesh, which is considered to be the most suitable fraction for environmental analysis (De Vivo et al., 2004). Following homogenization of the <2 mm grain size fraction, at least 30g of each routine and field duplicate sample was placed in two small plastic bags for laboratory analysis, and the remaining amount was stored for future reference.

The analysis were conducted in the Bureau Veritas Analytical Laboratories Ltd. (Vancouver, Canada), where they determined by a combination of ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy), following a hot aqua regia digestion, the concentrations of 53 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V,W, Y, Zn and Zr.

The detection limits are quite low, as it is possible to see from Table 1.1.

For quality controls, precision and accuracy of the analysis were calculated (Table 1.1).

Table 1.1: *Table reporting precision and accuracy for the analytical results of 3535 samples of Campania region.*

Element	Units of measure	Detection limit	Accuracy %	Precision %
Al	%	0.01	4.5	3.8
Ca	%	0.01	4.1	3.3
Fe	%	0.01	2.6	4.5
K	%	0.01	3.1	1.5
Mg	%	0.01	2.7	3.6
Na	%	0.001	7.2	4.2
P	%	0.001	3.7	6.8
S	%	0.02	2.8	6.2
Ti	%	0.001	6.8	7.9
Ag	µg/kg	2	4.3	7
As	mg/kg	0.1	2.6	2.7
Au	µg/kg	0.2	5.0	8.7
B	mg/kg	1	0.4	8.2
Ba	mg/kg	0.5	4.3	5.6
Be	mg/kg	0.1	6.9	11.1
Bi	mg/kg	0.02	8.5	16.2
Cd	mg/kg	0.01	5.2	6.9
Ce	mg/kg	0.1	9.2	7.1
Co	mg/kg	0.1	5.5	8.9
Cr	mg/kg	0.5	5.2	4.6
Cs	mg/kg	0.02	3.4	4.3
Cu	mg/kg	0.01	4.8	8.4
Ga	mg/kg	0.1	5.0	5.2
Hf	mg/kg	0.02	18.8	7.5
Hg	µg/kg	5	9	17.7
La	mg/kg	0.5	10.1	6.2
Li	mg/kg	0.1	4.3	5.2
Mn	mg/kg	1	2.7	3.8
Mo	mg/kg	0.01	6	4.4
Nb	mg/kg	0	15.4	14
Ni	mg/kg	0.1	3.5	3.7
Pb	mg/kg	0.01	4.8	3.3
Rb	mg/kg	0.1	3.8	2.5
Sb	mg/kg	0.02	14.7	3.5
Sc	mg/kg	0.1	7.2	4.2
Se	mg/kg	0.1	4.3	10.4
Sn	mg/kg	0.1	5.7	4.7
Sr	mg/kg	0.5	6.9	5.1
Te	mg/kg	0.02	5.1	9.1
Th	mg/kg	0.1	6.2	5.6
Tl	mg/kg	0.02	3.6	3.5
U	mg/kg	0.1	6.9	2.2
V	mg/kg	2	4.6	10
W	mg/kg	0.2	5.6	4.8
Y	mg/kg	0	8.4	5.4
Zn	mg/kg	0.1	3.6	4.7
Zr	mg/kg	0.1	3.6	18

Precision of the analysis was calculated using the results of 29 in-house replicates, and 5 blind project duplicates using the Relative Percentage Difference (% RPD):

$$\% \text{ RPD} = [\,|S-D|/(|S+D|/2)]*100$$

Where, S = measure of the original sample
D = Measure of the replicate sample.

The % RPS must be as close as possible to the zero value. Median value of the Relative Percentage Difference, RPD is 1.3%.

Accuracy (median value 2.2%) was determined using in-house reference materials (STD DS9, STD DS10, STD DS11, STDOXC109), with the following formula:

$$[(|X - TV|) / TV] \times 100$$

Where, X = analytical result of the *standard sample* measured by the laboratory
TV = real value of the *standard sample.*

Method detection limits for Al, Ca, Fe, K, Mg, Na, P, S and Ti range from 0.001 wt.% (Na, P, Ti) to 0.02 wt.% (S) and from 0.01 mg/kg to 5 mg/kg for all the other elements (Buccianti et al., 2015).

1.5 Statistical analysis

Table 1.2 includes the main statistical parameters of the 53 analyzed elements (number of samples, maximum, minimum, mean, geometric mean, median, mode, standard deviation).

For each element have been created:

- Box plots
- Cumulative frequency curves
- Histograms

By using these graphics, the study of the distribution is easier. On the box plot is possible to evaluate altogether the central tendency (median), the dispersion of the data (the interquartile range, represented by the rectangle), and the presence of possible anomalous values, represented by extreme values on the graph.

Table 1.2: *Table reporting the main statistical parameters (number of samples, minimum ,maximum, mean, geometric mean, median, mode, standard deviation, root mean square, variance, standard error, skewness, kurtosis) for the 52 analyzed elements in the top soil samples of Campania region. Ge, In, Nb, Pd, Pt and Re are not in the table, because more than 50% of the samples is below detection limit.*

Element	Units of measure	Samples number	Min	Max	Mean	Geom. mean	Median	Mode	Dev.st.	RMS	Variance	St. Er.	Skew ness	Kurtosis
Al	%	3535	0.21	9.47	4.01	3.55	4.09	5.56	1.69	4.35	2.87	0.028	0.027	-0.76
Ca	%	3535	0.080	29.5	3.59	2.34	2.25	2.21	3.70	5.16	13.7	0.062	2.36	6.99
Fe	%	3535	0.16	15.5	2.48	2.34	2.48	2.81	0.80	2.61	0.64	0.013	1.26	19.44
K	%	3535	0.040	6.82	1.41	0.95	0.95	0.37	1.26	1.89	1.58	0.021	1.39	1.18
Mg	%	3535	0.070	10.5	0.73	0.58	0.57	0.36	0.74	1.04	0.55	0.012	5.12	36.95
Na	%	3535	0.002	2.95	0.37	0.18	0.27	0.070	0.36	0.52	0.13	0.006	1.21	1.61
P	%	3535	0.005	1.66	0.17	0.13	0.13	0.090	0.13	0.21	0.016	0.002	2.17	11.81
S	%	3348	<0.02	0.66	0.043	0.032	0.040	0.030	0.040	0.059	0.002	0.001	6.09	65.65
Ti	%	3535	0.001	0.29	0.11	0.081	0.12	0.18	0.061	0.13	0.004	0.001	-0.27	-0.73
Ag	µg/kg	3395	<2.00	8132	183	92	92	100	312	361	97045	5.35	9.53	182
Au	µg/kg	3146	<0.2	1279	14.7	5.50	4.70	2.10	47.4	49.6	2242	0.84	13.7	270
Hg	µg/kg	3150	<5.00	6775	111	64.7	58.0	45.0	213	240	45171	3.79	14.4	365
As	mg/kg	3535	0.60	164	12.4	11.0	12.0	7.00	7.37	14.5	54.4	0.12	6.24	90.45
B	mg/kg	3535	1.00	98.0	14.4	11.7	11.0	10.0	9.15	17.1	83.7	0.15	1.36	3.22
Ba	mg/kg	3535	9.00	2631	392	316	367	45.0	230	454	52691	3.86	1.04	4.33
Be	mg/kg	2099	0.20	16.9	4.44	3.72	4.50	4.40	2.25	4.98	5.08	0.049	0.41	0.74
Bi	mg/kg	3198	0.03	11.8	0.47	0.41	0.44	0.48	0.41	0.62	0.17	0.007	12.5	256
Cd	mg/kg	3387	<0.01	11.1	0.49	0.36	0.36	0.20	0.54	0.73	0.29	0.009	8.10	121
Ce	mg/kg	1768	2.30	282	76.1	66.1	76.7	88.7	34.8	83.6	1208	0.83	0.70	2.25
Co	mg/kg	3535	0.50	79.0	10.5	9.28	10.2	3.00	5.09	11.7	25.9	0.086	1.65	12.25
Cr	mg/kg	3535	<0.5	808	17.7	13.2	17.7	5.00	26.6	31.9	708	0.45	16.5	374
Cs	mg/kg	1768	0.33	35.7	10.3	7.61	11.6	1.24	5.82	11.8	33.8	0.14	-0.15	-0.66
Cu	mg/kg	3535	2.51	2394	110	66.1	63.1	9.00	159	194	25292	2.67	5.44	43.51
Ga	mg/kg	3265	0.60	21.30	8.23	7.59	8.20	4.00	3.14	8.81	9.86	0.055	0.28	-0.23
Hf	mg/kg	1768	<0.02	3.75	0.34	0.25	0.27	0.28	0.32	0.47	0.10	0.008	3.77	24.33
La	mg/kg	3535	0.90	162	41.4	37.2	41.0	41.0	17.8	41.0	318	0.30	0.70	2.62
Li	mg/kg	1766	2.00	51.6	20.7	19.5	20.1	20.9	7.36	22.0	54.1	0.18	0.58	0.68
Mn	mg/kg	3535	77.0	7975	858	794	775	373	445	967	198325	7.49	5.54	57.0
Mo	mg/kg	3535	0.060	62.2	1.51	1.24	1.24	2.00	1.59	2.19	2.53	0.027	18.8	624
Nb	mg/kg	1768	0.010	24.3	6.69	4.33	6.57	0.59	4.66	8.16	21.7	0.11	0.53	-0.10
Ni	mg/kg	3535	0.50	101	16.2	1.12	14.7	17.0	11.1	19.6	123	0.19	2.42	9.88
Pb	mg/kg	3535	3.12	2052	74.7	54.2	54.4	43.0	93.3	119	8701	1.57	7.58	96.8
Rb	mg/kg	1768	4.20	531	113	86.9	107	221	69.3	133	4808	1.65	0.42	-0.16
Sb	mg/kg	3300	<0.02	42.8	1.08	0.71	0.66	0.50	1.92	2.20	3.67	0.033	11.3	197
Sc	mg/kg	3239	0.30	12.9	2.59	2.28	2.30	1.80	1.37	2.93	1.88	0.024	1.46	3.17
Se	mg/kg	3141	<0.1	2.4	0.41	0.32	0.40	0.050	0.25	0.49	0.06	0.005	1.43	5.38
Sn	mg/kg	2099	0.20	126	3.97	2.95	3.30	2.80	4.38	5.91	19.2	0.10	12.7	304
Sr	mg/kg	3535	4.60	1153	178	141	153	39.0	111	210	12382	1.87	1.12	2.72
Te	mg/kg	3150	<0.02	0.56	0.05	0.04	0.04	0.010	0.04	0.06	0.001	0.001	2.63	18.1
Th	mg/kg	3535	0.30	59.1	12.6	10.7	12.3	9.00	6.50	14.2	42.2	0.11	1.02	2.97
Tl	mg/kg	3348	0.050	69.0	1.41	1.15	1.35	1.00	1.41	1.99	1.98	0.02	33.6	1590
U	mg/kg	3369	0.050	23.7	3.37	2.69	3.00	2.00	2.15	4.00	4.61	0.04	1.42	4.84
V	mg/kg	3535	5.00	224	66.2	58.9	60.0	50.0	30.4	72.9	922	0.51	0.56	-0.22
W	mg/kg	3378	0.050	12.2	1.01	0.76	1.00	1.00	0.64	1.19	0.41	0.011	3.08	36.8
Y	mg/kg	1768	1.07	151	15.4	14.1	14.1	12.7	7.17	16.9	51.4	0.17	5.62	80.2
Zn	mg/kg	3535	11.4	3211	120	98.3	91.1	48.0	120	170	14504	2.03	9.10	160
Zr	mg/kg	1768	270	51229	29.0	19.1	23.8	20.9	26.0	39.0	679	0.62	2.86	15.8

1.6 Cartographic elaboration

For each of the 53 analyzed elements, have been elaborated:

- Dot maps

- Interpolated maps
- *Background/Baseline* maps
- Distribution maps showing the overcomings of the contamination threshold values (CSC) established by the Italian legislation (D.Lgs. 152/06) for the potentially toxic elements
- Distribution maps of the *factor scores* for the four elements associations by *R-mode* factor analysis.

In this thesis will be discussed only the maps of the 15 potentially toxic elements listed by the D.Lgs152/06, that will be used for the further elaborations.

Dot maps are useful for having a representation of the real concentrations distributions at the moment of the sampling. The maps have been classified in intervals of concentration, chosen analyzing the cumulative curves. Seven were the reference percentiles for establishing the intervals: 10, 25, 50, 70, 90, 95, 98. These percentiles were used if no significant breaks of slope were observed in the cumulative distribution, otherwise the concentration corresponding to the break of slope was used for identifying the interval.

The *interpolated maps* are useful for a graphical representation of geochemical data. While dot maps shows the real concentrations in the sampling sites, the interpolated maps are based on probabilistic assumptions on the concentration values in the sites where there are no samples. The interpolated maps give not a real value, but delineates the possible trends/patterns to be then interpreted based on the geological and environmental situations in the analyzed area. As much as complicate it might be, the mathematical algorithm at the base of the interpolation method cannot predict the geochemical concentration in case of particular geological conditions or specific anthropic contamination.

For the interpolation we chose the *Inverse Distance Weighted* (IDW) algorithm, associated to a new methodology developed for recognizing the different populations in a geochemical database, the *Multifractal Inverse Distance Weighted* (MIDW), based on the application of fractal and multifractal geometry. Conventional interpolation methods, such as *kriging* and ordinary IDW, smooth the data and loose the information about the local variability, that in geochemistry is fundamental to locate geological features. Multifractal interpolation is a new method that preserves high frequency information, which is otherwise lost. The method (Cheng, 1999; Cheng et al., 2000) takes into account both spatial association and local singularity. Spatial association represents a type of statistical dependency of values at separate locations; these indexes (covariance, autocorrelation and semivariogram) have been used to characterize the local structure of surfaces and, in *kriging*, for data interpolation. Singularity is an index representing the scaling dependency from a multifractal point of view, which characterizes how the statistical behavior of a spatial variable changes as the measuring scale changes. Spatial association and scaling are two different aspects of local structures and surfaces. Both should be taken into account in data interpolation and surface mapping of geochemical variables. A conventional weighted

average technique such as *kriging* and ordinary IDW smooth the local variability of the geochemical data, whereas MIDW creates a geochemical map in which information about the local variability and structure is retained (Lima et al., 2008).

The classification of the pixels in concentration intervals in the MIDW interpolated maps was assigned using the fractal concentration–area (C–A) method. By means of the C-A plot, we can subdivide the interpolated map in "*pixel populations*" and assign to each population a different color. Those colors on the map should allow to distinguish units with different geochemical characteristics. In the C-A plots, the pixel concentration values (ρ) are plotted against the cumulative area [A(ρ)] on log–log scale. These plots characterize not only the frequency distribution of pixel values, but also the spatial and geometrical properties of the features reflected by pixel zones in the image. Area concentration [A(ρ)] with element concentrations greater than ρ show a power-law relation. If the geochemical surface is fractal, a single straight line relationship would occur, whereas for a multifractal surface, values will fall on several straight lines. The breaks between straight-line segments on this plot and the corresponding values of ρ, have been used as cut-offs to separate geochemical values into different components (Fig. 1.5), representing different causal factors, such as lithological difference and geochemical processes (e.g. mineralizing events, surficial geochemical element concentrations, surficial weathering) (for more details see Cheng et al., 1994).

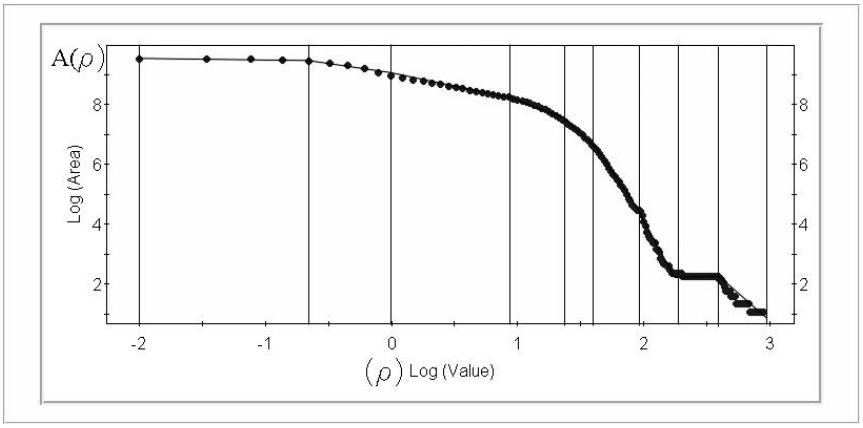


Fig. 1.5: *Example of C-A plot in logarithmic scale, where the concentration values in association with each pixel are on the x-axis (ρ), while the cumulate corresponding areas A(ρ) are on the y-axis.*

The *background/baseline* maps have been obtained with the S-A method.

Before establishing that a concentration value is anomalous, it is necessary to know which is the natural concentration value of the elements in the area due to the geological setting (*background*) or to anthropic activities (*baseline*). To define the *background* value of an element in a soil, it is necessary to determine its geogenic concentrations, in a completely uncontaminated place, such as the C horizon of a stratified soil, that is at a certain depth from the surface, sufficently "protected" from the superficial contamination. In areas influenced by diffuse urban pollution, the local anomaly threshold is referred to the *baseline* (Fig. 1.6). In the realised maps we consider the regional anomaly threshold, which is,

basically, coincident with the upper limit of the natural *background* concentration interval (Albanese et al., 2008).

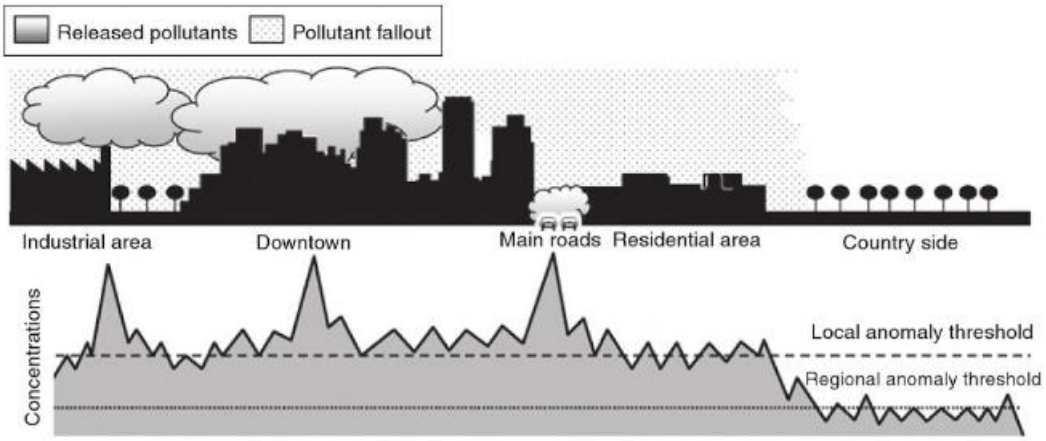


Fig. 1.6*: Regional and local anomaly threshold applied to an urban environment. The concentration graph shows the influence of anthropogenic sources (industrial area, downtown and main roads) on pollutant distribution in soils (from Albanese et al., 2008).*

The GeoDas program has been implemented for the S–A method, a *fractal filtering technique*, based on a Fourier spectral analysis (Cheng, 1994; Cheng et al., 1996; 1999; 2000; Cheng, 2001, Fig. 1.7), used to separate anomalies from background values. It also uses both frequency and spatial information for geochemical map and image processing. The basic geological assumption for the S–A method is that a geochemical field or image generated by specific geological processes may be discriminated in terms of its fractal properties. The scale invariant property of most geological processes (e.g. erosion processes, mineralizing events, magnetic field of the earth's crust, distribution of earthquakes and volcanic eruption) often show ''self-similarity'' or ''self-affinity''. These properties can be measured in both the frequency and the spatial domain (Turcotte, 1997). In the spatial domain, scaling properties are related to the spatial geometry of patterns, the histogram distribution of values, and the changes in shape corresponding to changes in value, as used in the MIDW interpolation method described earlier. In the frequency domain, such properties can be represented by means of power spectra (Lewis et al., 1999; Cheng et al., 2000). The properties of a power spectrum in the frequency domain are used to define the fractal filter, by which divide the power spectrum into components characterized by similar scaling properties. It is an irregularly shaped filter, due to the anisotropic and usually complex intrinsic structure of the geochemical data. The filter can be used to identify anomalies from the background, and to extract other meaningful patterns from the original map (see Xu and Cheng, 2001 for more details). Fractal filters are defined in Fourier space by applying the fractal C–A model (Cheng et al. 1994) to the power spectrum of the processed geochemical field. 2-D Fourier transformation and inverse Fourier transformation provide the foundation for converting the geochemical field (map) between spatial and frequency domains. Fourier transformation can convert geochemical values into a frequency domain in which different patterns of frequencies (high-low frequencies) can be

identified. The signals filtered with certain ranges of frequencies can be converted back to the spatial domain by inverse Fourier transformation.

The MIDW interpolated maps have been converted by means of Fourier transformation in the frequency domain and each value of the power spectrum has been plotted in logarithmic scale. In the plot, a straight line divided in two portions the plot, to obtain two subsets of frequencies: low frequencies (*background/baseline*) and high frequencies (*anomalies*) power-spectra. The vertical line on each plot (Fig. 1.7) marks the cutoff applied in order to generate the corresponding filter based on the power spectrum and the two classes of frequencies chosen. Applying these filters to the Fourier transformed signals and converting them back to the space domain yield two different images. The one with the high power-spectrum filter applied will represents the background geochemical patterns whereas the other with the lower power-spectrum filter applied represent the anomalous signals. The anomaly maps were not reported in the geochemical Atlas of Campania region. Once again the colour-scale classification based on the C–A fractal method allows areas with different background values to be better delimited based on the different populations (with the same fractal properties) identified using the C–A plot (Lima et al., 2008).

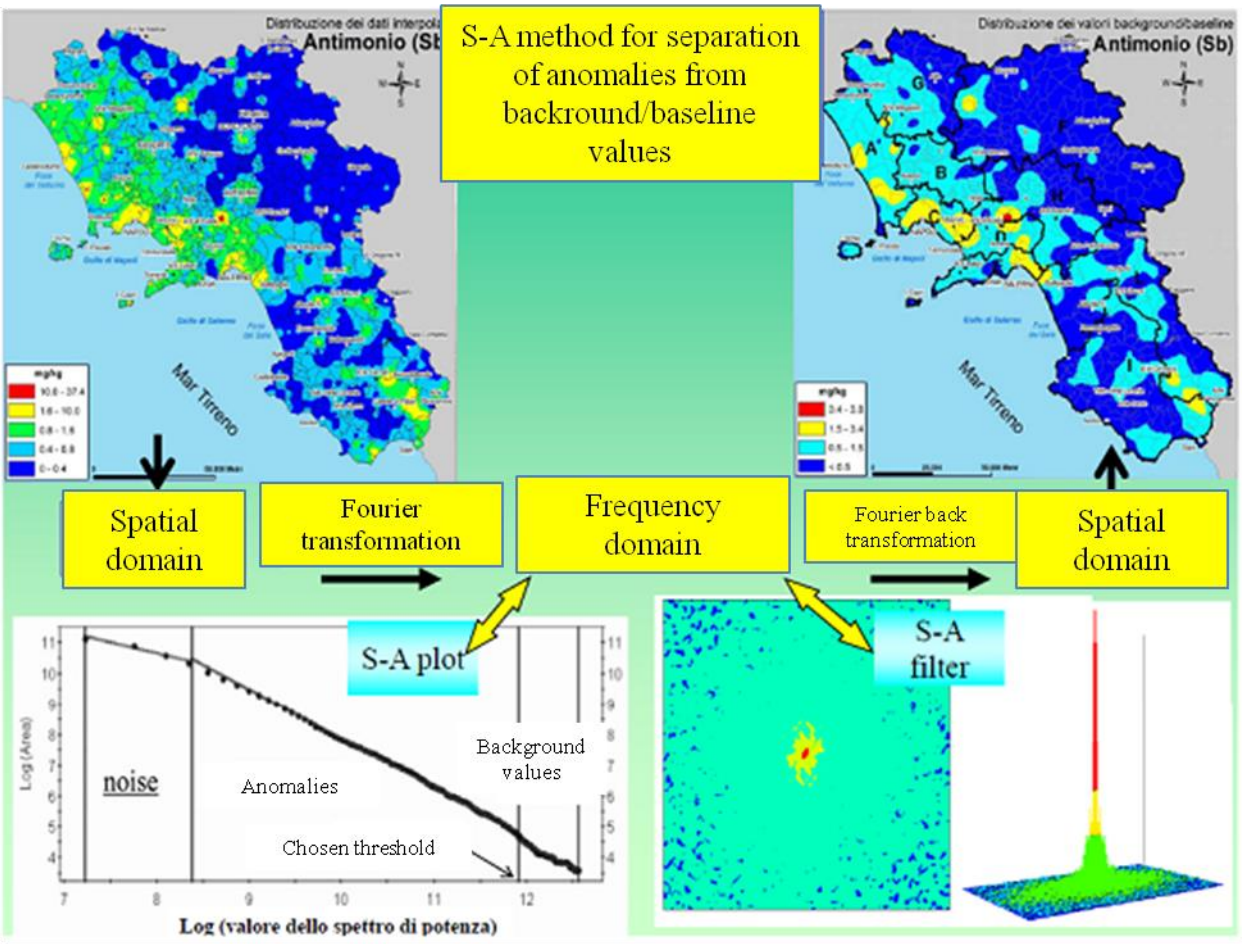


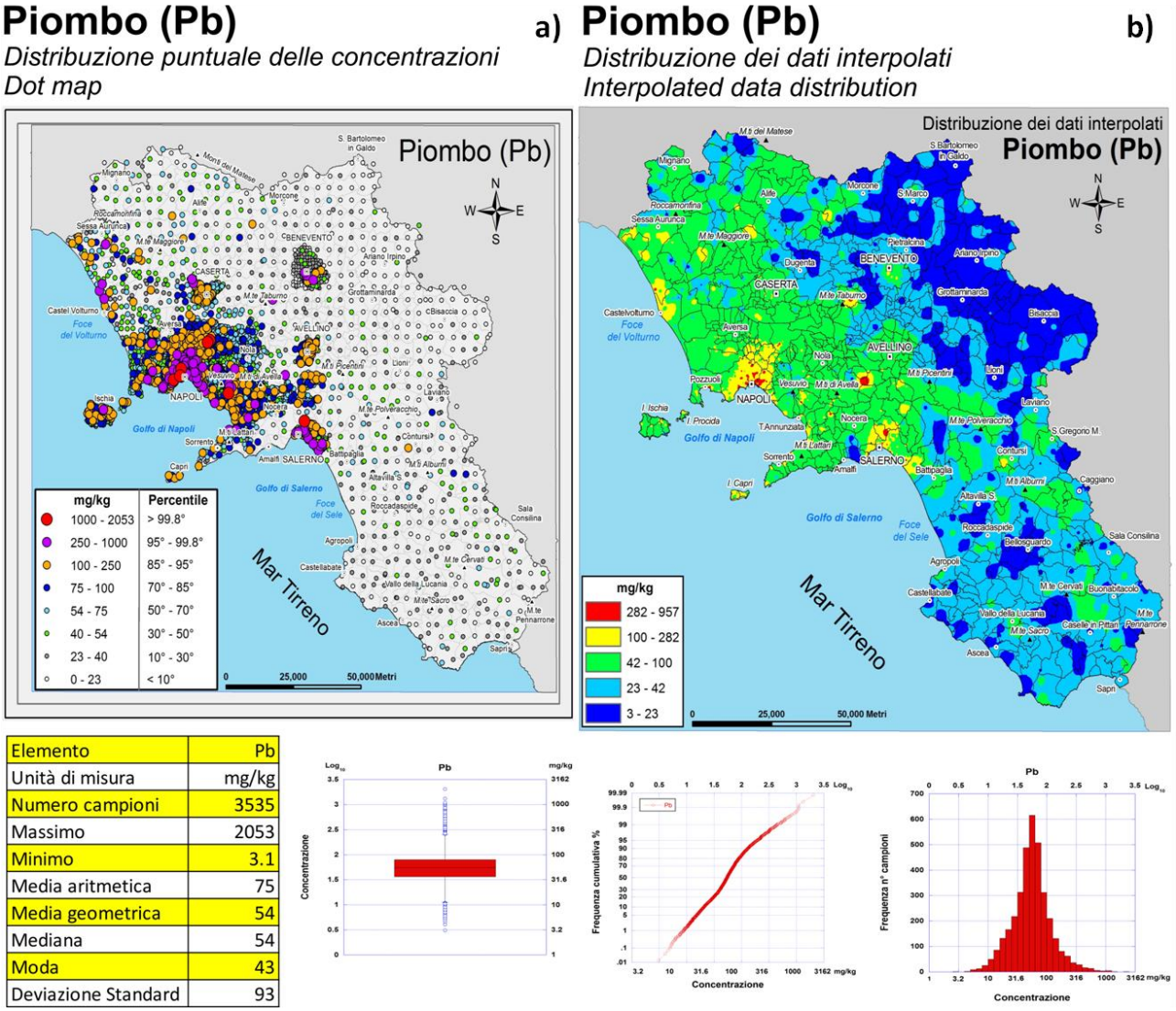
Fig. 1.7*: Synthetic scheme for explaining the S-A fractal filtering technique, used for separating the baseline values from anomalies (see text for explanation).*

The maps highlighting the concentrations above the *contamination threshold values (CSC)* have been produced for the 15 potentially toxic elements for environment and human health established by the D.Lgs. 152/06 (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn). For these elements they defined the CSC threshold values in the soils that, if above the limit for Residential or Commercial/Industrial use, requires a follow-up risk assessment.

The dot maps of those elements have been reclassified, subdividing the concentration values in three intervals, using the CSC for residential/public use of soil and for industrial/commercial use. It was possible to visualize for each sampling site the onmes with concentrations higher than the threshold values for each element.

1.7 Description of the 15 potentially toxic elements

For the purpose of this thesis, in this paragraph we will explain the properties, the effects on human health, and the distribution in Campania soils of the potentially toxic elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V e Zn). Those elements are also known as trace elements, because their concentrations in rocks are commonly < 0.1%. For the descriptions of all the elements, we refer to *the Environmental geochemical Atlas of Campania soils* (De Vivo et al., 2016); the maps have been uploaded in the attached DVD. In Figures 1.8 and 1.9 examples of dot, interpolated, baseline and CSC intervention limits maps, accompanied by statistical graphs, are shown.



Elemento	Pb
Unità di misura	mg/kg
Numero campioni	3535
Massimo	2053
Minimo	3.1
Media aritmetica	75
Media geometrica	54
Mediana	54
Moda	43
Deviazione Standard	93

Fig. 1.8: *a) Examples of dot map, box plot and statistical parameters for Pb; b) Examples of interpolated map, histogram and cumulative curve for Pb.*

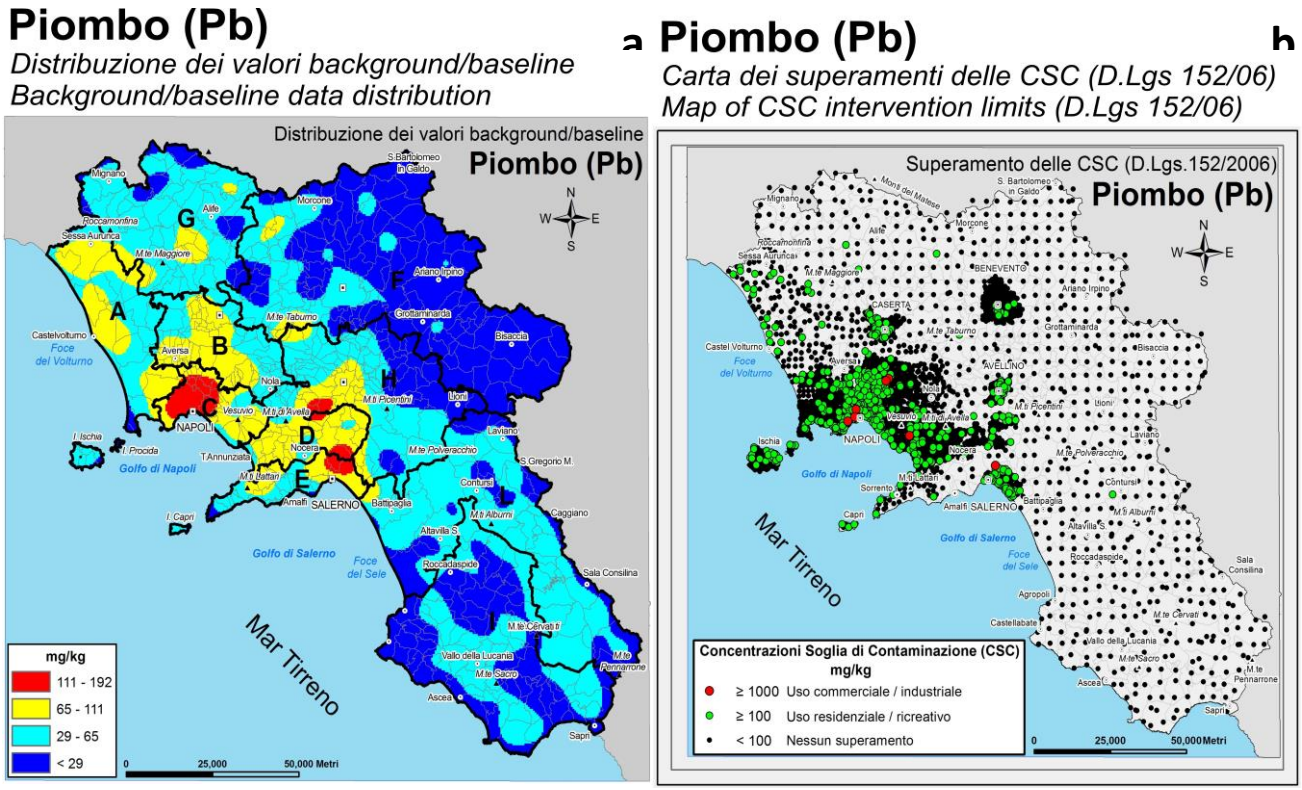


Fig. 1.9: *a) Example of background/baseline map for Pb; b) Example of CSC overcoming map for Pb.*

1.7.1 Arsenic (As)

1.7.1.1 Properties, applications and effects on human health

Arsenic (As, atomic number 33) is a trace element often considered a 'heavy metals' in the environmental literature, although it has predominantly a non-metallic character. It appears in oxidation states -3, +3 and +5, and has only one naturally occurring isotope (^{75}As). Arsenic has a strongly chalcophile character, and its occurrence in the natural environment is most often associated with its own sulphur mineral arsenopyrite (FeAsS), and with other sulphides and sulphoarsenides. In silicates, As^{3+} can, to a certain extent, substitute for Fe^{3+} and Al^{3+}, and thus trace amounts of As can occur in common silicates, like feldspar. In relation to agricultural soil, is probably the ability of As^{5+} to replace P^{5+} in phosphate minerals, such as apatite, which are often used as mineral fertilisers. Anomalous contents of As are correlated to epithermal and mesothermal ore (especially gold) deposits and it is generally enriched in hydrothermal alteration zones. Most common rock types contain low concentrations of As – between 0.5 mg/kg (sandstone) and 3 mg/kg (granite, granodiorite). Exceptions are shale and schist (13 mg/kg) and coal (10 mg/kg). Coal that is strongly enriched in As (several hundred mg/kg) is known, and burning of such coal has caused severe environmental and health problems. In soils and sediments, the mobility of As is not really high, because of its tendency to coprecipitate with Fe and Mn oxy-hydroxides, as well as with clay and organic matter.

The main sources of As in the environment are volcanic (hydrothermal activities) and anthropic activities (coal combustion, geothermal centers, agriculture, Cu, Pb, Zn smelting). Arsenic is intensively used in many herbicides, insecticides and fungicides, and it promotes growth in some animals, so it is used as food in farming. If sewage coming from these farms is spread as fertilizer, high levels of As can be transferred to soil.

Arsenic is known as the "king of poison" in the human history. Humans take-up As via water and food. Luckily, with the exception of some kinds of seafood, plants usually avoid the uptake of As from soil, and there are only a few plants that accumulate As (e.g., radish, rice).

Thus, As does not enter the food chain easily. High As concentrations in ground water, usually related to specific geological settings, pose the greatest risk to humans. Such settings are known in several parts of Europe.

1.7.1.2 As distribution in top soils of Campania region

Arsenic content in the analysed samples varies from 0.6 mg/kg to 164 mg/kg, with a median value of 12 mg/kg. These concentrations are higher than the Italian values (2.67-63 mg/kg), while the European top soils show a wider concentration range (0.32-282 mg/g), but a lower median value (6 mg/kg) (De Vivo et al., 2008a, 2006a).

The As dot map shows that only 10% of the samples have As concentrations >20 mg/kg (90° percentile); those are distributed around the volcanic areas, but with some high *hot spots* (>99° percentile) in the Solofra basin, Vallo di Diano and in the soth-western part of Roccamonfina.

The interpolated map clearly shows how the lowest As concentration (<11 mg/kg) are localized along the Apennine belt, in the inner areas of Benevento and Avellino provinces, and on the Cilentan coastline. Intermediate concentrations (11-25 mg/kg) can be found in wide areas well influenced by volcanic deposits (Napoli and his province, up to Avellino and Caserta, Domitian coast, and the southern Appennine belt, from Picentini Mounts to Cervati Mountain). Areas of limited extension with high concentrations (>25 mg/kg) can be locally found in proximity of Somma-Vesuvio, Campi Flegrei and Roccamonfina volcanic apparatus, due to volcanic soils and hydrothermal activity (Cicchella et al., 2005). Other areas where the high As contents are most probably due to anthropogenic activities, are developed on silico-clastic and carbonate sediments of the Agro-Nocerino-Sarnese area, especially in the Solofra basin, and Vallo di Diano, among Buonabitacolo and Sapri.

The *background/baseline* map confirms that the regional territory can be divided in two macro-areas, with different backgrounds depending on the geo-litological settings. The majority of the regional territory, not influenced by volcanic sediments, shows values <13 mg/kg. The areas interested by volcanic activity or with a pyroclastic overlay have values ranging between 13 and 32 mg/kg, compatibly with the natural *background* for volcanic soil. The high concentrations (32-39 mg/kg) found in the northern part of Napoli, in Vallo di

Diano and Agro-Nocerino-Sarnese areas are influenced by anthropic activities, such as intense farming practices that make a wide use of fertilizers and pesticides.

Of the totality of the analysed samples, 10% overcomes the CSC value for residential use (20 mg/kg), as established by the D.Lgs. 152/06, while 0.6% overcomes the CSC value for industrial/commercial use (50 mg/kg). While the overcoming for residential use is compatible with the *background* concentration values for volcanic soils, the industrial and commercial areas with intolerable values are probably influenced by anthropic activities, exluding the Phlegrean area, where it is correlated with hydrothermal activity.

1.7.2 Beryllium (Be)

1.7.2.1 Properties, applications and effects on human health

Beryllium (Be, atomic number 4) is a rare alkaline earth metal. The small size of the Be^{2+} ion (0.35 Å) implies that Be behaves incompatibly during early magmatic fractionation. This means that Be has a tendency to concentrate in late stage igneous rocks, especially in evolved granite and pegmatite (5-10 ppm). Beryllium is most highly concentrated in beryl and chrysoberyl, but the more abundant micaceous minerals, such as muscovite, are responsible in terms of its distribution in the Earth's upper continental crust and especially in soil (Wedephol, 1978). The Be concentration in sedimentary rocks generally reflects the presence of micaceous material and secondary clays. When released during weathering, Be binds to clay or humic material co-precipitates with Fe-Mn hydroxides. Clay minerals weathered from alkaline igneous rocks can show unusually high Be concentrations (100 ppm), while values of 60 ppm have been recorded in bauxite. Its strong affinity for organic matter is reflected in the high Be content of most coal deposit (Ure and Berrow, 1982).

Beryllium has many uses that may contribute to anthropogenic pollution in electronics, nuclear and aerospace industry (e.g., brake systems of airplanes, as window material for X ray tubes, accessories for computers). Coal combustion is an important source of Be transfer to the atmosphere and environment.

Beryllium is non-essential for life and Be^{2+} is toxic to humans and animals. Virtually all Be compounds exhibit significant pulmonary toxicity, the main form of exposure being through inhaled dust and vapors. Furthermore, Be has been added as carcinogenic substance in Group 1 from IARC.

1.7.2.2 Be distribution in top soils of Campania region

The measured Be concentrations varies between 0.2 mg/kg to 16.6 mg/kg, with a median value of 4.5 mg/kg. These concentrations are comparable with those observed in the Italian

top soils (0.3-15.6 mg/kg), but the median value is higher than the Italian one (2.3 mg/kg) (De Vivo et al., 2008a). In most of the European top soil samples the measured Be concentration is below 2 mg/kg, and the maximum concentration is 18.4 mg/kg (De Vos et al., 2006).

From the dot map it is possible to observe that only 10% of the samples have Be concentration >8.5 mg/kg. Those samples are located in Salerno and Agro-Nocerino-Sarnese areas, Solofra basin, Sorrento peninsula, Phlegrean and Domitian areas, and around Caserta province. The same areas contain the 1% of the samples with Be >10 mg/kg (99° percentile), representing the threshold value for soils designated to industrial/commercial use; spotted values are sited in Cilento and Vallo di Diano areas as well. The remaining territory has generally low values, <4.5 mg/kg.

In the interpolated map, two regional *trends* are highlighted; the first one with values <4 mg/kg controlled by silico-clastic and carbonate lithologies (internal Apennine areas of Benevento and Avellino provinces, and the Cilento coast); the second one with Be > 4 mg/kg corresponding with the potassic-alkaline rocks. The highest concentrations, > 7 mg/kg, are located far away from the Campanian volcanic apparatus. This is probably due to the tendency of Be to concentrate in the late magmatic products, ejected in the pyroclastic *fall out* during explosive events, mainly characteristic of Somma-Vesuvio volcano. The resulting deposits cover the western part of the Appenine belt, along the Lattari Mounts, Sorrento peninsula, Agro-Nocerino-Sarnese area and Solofra basin. Limited *hot spots* are found also in the Vallo di Diano area.

The *background/baseline* map shows that most of the Campanian top soils have Be values < 5 mg/kg. Wide areas with Be < 2 mg/kg correspond to silico-clastic lithologies. High values can be found around Somma-Vesuvio, Campi Flegrei and Roccamfina volcanoes. The presence of Be in Campanian soils due to anthropic contribute is very unlikely, because the diffused activities does not lead an intake of this element in the environment.

Almost all of the Be top soils values overcome the CSC values for residential use (2 mg/kg), and only the 18% of the samples is lower. The threshold established by the D.Lgs. 152/06 is probably too low, and does not take into account the natural *background* values, due to the volcanic disposition of the area, that cannot be modified. Furthermore, the 1% of the samples overcoming the CSC for industrial/commercial use (10 mg/kg) is probably part of the natural *background* values.

1.7.3 Cadmium (Cd)

1.7.3.1 Properties, applications and effects on human health

Cadmium (Cs, atomic number 48) is a trace, chalcophile element that most commonly occurs as a substitute for Hg, Cu, Pb and Zn in sulphide minerals. It is also found in trace

amounts in some silicate minerals, such as biotite and amphibole. In sedimentary rocks the higher levels are found in shale (0.25 ppm), especially organic-rich sediments, and in marine manganese nodules and phosphorite; lower levels occur in igneous and metamorphic rocks (granite typically 0.09 ppm, basalt 0.13 ppm), sandstone and limestone. Elevated Cd values are generally indicative of sulphide mineralization, associated with Pb and Zn (Sedex and VHMS mineralization). The sulphate and carbonate of Cd are less soluble than those of Zn, but humic substances, clay minerals and Fe oxide adsorb and selectively bind Cd, controlling Cd distribution and possibly causing Cd anomalies in sediments.

In the surface environment, Cd can be quite mobile in oxidizing conditions at a pH < 8 (Brookins, 1988). Under a higher pH (e.g., limestone areas, karst), Cd will precipitate with carbonates. Its environmental mobility is limited somewhat by its tendency to sorb to clay minerals or organic matter and to co-precipitate with Fe- and Mn-hydroxides. In the soil, Cd activity is strongly controlled by pH; it is more mobile in acidic soil within the pH range of 4.5 to 5.5, and its solubility is largely controlled by organic matter and sesquioxides. In alkaline soil, Cd is rather immobile and precipitation of Cd compounds occur.

Cadmium is used extensively in industrial processes. Of these, electroplating and Ni-Cd battery, paint, ink and plastic manufacture are of greatest importance. Sewing sludge and leaching of waste from these processes may have an impact on surface water chemistry. Cadmium tends to volatilize at high temperatures, providing a mechanism for its entry into the hydrological cycle via atmospheric deposition downwind of industrial regions. The increasing use of Zn in phosphate fertilizers may lead to remarkable Cd concentrations.

Cadmium has no essential biological function. It is toxic to humans through the inhalation of dust, causing lung damage, and may cause cancer from long-term exposure (WHO 1996); it is also teratogenic and embryocidal (Smith 1999).

Cd is one of the interesting elements for which there is the possibility of a strong bioaccumulation in soil, without any human contribution. It tends to accumulate in plants and aquatic biota, with consequent problems of toxicity.

1.7.3.2 Cd distribution in top soils of Campania region

Cadmium content in the analyzed samples varies between <0.01 mg/kg ti 11.06 mg/kg, with a median value of 0.36 mg/kg. The measured values of Campania region's top soils are higher than the Italian ones (0.06-3.03 mg/kg, median value 0.18 mg/kg) (De Vivo et al., 2008), but in line with the European ones (0.145-14.2 mg/kg), that have a lower median value (0.15 mg/kg) (De Vos et al., 2006).

The dot map shows that only 2.5% of the samples have Cd concentration >2 mg/kg, the threshold value for residential use of soil. These samples are located in the urban areas of Napoli, Agro-Nocerino-Sarnese, Caserta, Salerno, Vallo di Diano, and in proximity of Matese Mounts.

The interpolated distribution map shows that the majority of the territory has concentration <0.6 mg/kg. Intermediate values, between 0.6 and 3.1 mg/kg, can be found in the urban areas of Napoli and Caserta. The highest concentrations, >3.1 mg/kg are located around the Matese Mounts and Cervati Mountain, where high levels of both Al and Be have been recorded. This particularly high levels of concentration may be correlated to the presence of bauxite deposits, which presence give alcalinity to soils, leading the accumulation of Cd.

The *background/baseline* map show that most of territory has Cd values < 0.4 mg/kg, and almost everywhere Cd is lower than 1.5 mg/kg. These concentrations are compatible with the *background/baseline* values found in Neapolitan and Salerno provinces (0.5-0.68 mg/kg, Cicchella et al., 2005; De Vivo et al., 2006). Some small area with values >1.5 mg/kg is located in correspondence of calcareous lithologies of the Appennine belt.

The 2.5% of the sampled sites shows an exceed of the CSC value for soils destined to residential/public use (2 mg/kg), while there are no excess of the threshold for industrial/commercial use (15 mg/kg). Most of the highest concentrations are located in Neapolitan province, Salerno, Caserta, Benevento, Agro Nocerino-Sarnese and Vallo di Diano areas, and in proximity of Matese Mountain.

1.7.4 Cobalt (Co)

1.7.4.1 Properties, applications and effects on human health

Cobalt (Co, atomic number 27) is a transition metal, with calcophile and siderophile properties. It forms rather several rare minerals and it is present as an accessory element in olivine, pyroxene, amphibole, mica, garnet and sphalerite. In early magmatic processes Co^{2+} substitutes for Fe^{2+} and Mg^{2+}, which are similar in charge and ionic radius, so Co is generally enriched in mafic and ultramafic relative to felsic igneous rocks (Wedepohl 1978). In sedimentary rocks, Co tends to vary with the Fe and Mn content and is concentrated in the finegrained fractions. Sandstone and carbonates have lower Co concentrations (<2 ppm); whereas arkose and greywacke are more enriched, with their Co concentrations usually reflecting the abundance of mafic minerals (Ure and Berrow 1982). Cobalt values of ca. 50 ppm are common in very fine-grained mudrocks, but Co concentrations in black shale are lower on average (Vine and Tourtelot 1970).

In surface environment Co mobility is controlled by sorption and co-precipitation with Fe- and Mn-oxides and hydroxides (Wedepohl, 1978). Hence Co is most mobile in the surface environment under acidic and reducing conditions, where the formation of high valency phases of Fe and Mn is inhibited.

Cobalt is widely used for industrial purposes both in the sector of aeronautical engineering as well as in the production of metals, ceramic, glass and cement. The main

anthropogenic sources are coal combustion, fertilizers, metal smelters (especially Cu, Ni) and Pb, Fe and Ag mining and processing.

Cobalt is a biologically essential element and is found in vitamin B-12. It can be toxic to humans at doses of 25 mg per day or more. Soluble cobalt compounds are suspected to be carcinogenic to humans by inhalation.

1.7.4.2 Co distribution in top soils of Campania region

Co content in the analyzed soils varies from 0.5 mg/kg to 79 mg/kg, with a median value of 10.2 mg/kg. The regional Co concentration are lower than its concentrations amongst the country (1.5-249 mg/kg, median value 12 mg/kg) (De Vivo et al., 2008), and European top soil values (maximum value 249 mg/kg, median value 7.78 mg(kg) (De Vos et al., 2006).

From the dot maps is it possible to observe that 90% of the sites have Co concentrations < 20 mg/kg, and only 1% of the samples have Co concentrations > 30 mg/kg. Those higher spots are located close to the urban areas of Napoli, Domitian shoreline, Agro-Aversano area.

The regional trends can be better identified from the interpolated maps. The coastal areas has Co contents < 13 mg/kg, with the only exception of the vesuvian area. Intermediate values, between 13 and 26 mg/kg are diffused in the southern area of the region and in the inner Appennine area. These areas are characterized by the presence of flysh with intercalated finedrained levels, that usually have the highest natural Co content (50 mg/kg). However the higher values, between 26 and 78 mg/kg, included with little spots in these areas, can represent an anthropic contribute, for illegal spill of appliances.

The *background/baseline* values account for < 16 mg/kg on a regional level, compatible with the natural *background* values of 3-14 mg/kg, evaluated by Cicchella e al. (2005). Some areas in the north-western sector is Co depleted (<8 mg/kg). Some areas in the eastern and southern part of the region have Co content >16 mg/kg. Only a small area, to the East of Morcone city, has a background value higher, between 21-35 mg/kg, corresponding with soils developed on silico-clastic sediments.

The CSC map shows that none of the sampled site overcomes the threshold values for industrial/commercial sites, while 10% overcomes the threshold for public/residential use (20 mg/kg). Those sites are in the province of Naples and, as explained before, in correspondence of flysh and silico-clastic lithologies, that could explain a natural enrichment of Co in the forming soils. However an anthropic contribute cannot be excluded.

1.7.5 Chromium (Cr)

1.7.5.1 Properties, applications and effects on human health

Chromium (Cr, atomic number 24) is a litophile transitional metal forming several minerals and present as an accessory element in several other, such as spinel, amphibole, mica, pyroxene and garnet. The trivalent ion Cr^{3+}, like other transition elements with intermediate radii, readily substitutes for Fe and Mg, and is partitioned into spinel and pyroxene during the earliest stages of crystal fractionation. As a result, Cr is enriched in ultramafic rocks (1000–3000 ppm), along with elements such as Ni and Co (Wedephol, 1978).

Chromium is abundant in sedimentary rocks as well, in primary detrital phases such as magnetite, ilmenite, and chromite ($FeCr_2O_4$), that are strongly resistant to weathering. Once released by weathering, Cr is a low mobility element. Trivalent chromium (Cr^{3+}) behaves much like Fe^{3+} and Al^{3+} and it thus accumulates with secondary oxides and clays. In soil, Cr behavior is governed by pH, Eh and organic matter; it tends to co-precipitate with Fe oxides, and to be absorbed by clay and organic matter. The dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} (that can be rather mobile) to Cr^{3+}, the rate of which increases with soil acidity (Kabata-Pendias 2001).

Chromium is a major component of steel alloys (10–26%) and used for coating steel as chrome plating. Chromates and dichromates, containing Cr^{6+}, are sometimes released in industrial effluents, especially from leather tanning and electroplating operations, and are highly poisonous and readily soluble. However, because of their powerful oxidizing properties they are rapidly reduced and sorbed by organic residues.

Chromium, once thought to be non-essential, is now known to be needed by the human body in small amounts for insulin action and the metabolism of proteins and carbohydrates. The toxicity of Cr depends strongly on its oxidation state. Soluble Cr^{3+} is considered relatively harmless, but Cr^{6+} is highly toxic, causing liver and kidney damage and acting as a carcinogen. The main exposure routes for Cr^{6+} are inhalation and dermal contact.

1.7.5.2 Cr distribution in top soils of Campania region

Chromium concentrations in the analyzed top soil samples are between <0.5 mg/kg and 808 mg/kg, with a median value of 14 mg/kg. Regional concentrations are lower than Italian (4-2340 mg/kg, median value 35 mg/kg) (De Vivo et al., 2008a) and European top soils concentrations (3-6230 mg/kg) (De Vos et al., 2006).

The dot distribution map shows that 99% of the measured soils have concentrations <70 mg/kg. The 1% of the higher values is concentrated in the urban area of Naples, and in the Agro-Nocerino-Sarnese area, in particular in the Solofra basin, with some *hot spots* in Salerno, Avellino and Vallo di Diano. The lower values are located in the campanian plain and along the coastline, while intermediate values, between 32 and 70 mg/kg, can be found along all the Appennine line.

The interpolated distribution map shows concentrations <34 mg/kg in almost all the region, and wide areas, in the campanian plain and along the coastline, with concentrations <18 mg/kg. Intermediate values, between 34 and 60 mg/kg are distributed in the inner Appennine areas, with flysh and silico-clastic lithologies. Some higher *hot spots* with values ranging between 60 and 114 mg/kg can also be found in the aforementioned areas and they are probably controlled by clay content. High *hot spots* located in the eastern part of Naples province, Sorrento peninsula, Agro-Nocerino-Sarnese area and Solofra basin are instead probably controlled by anthropic contribute, due to illegal spill of appliances, abandoned cars and various objects containing Cr.

The *background/baseline* values are < 32 mg/kg in almost all the region, and wide areas along the Campanian plain have concentrations < 16 mg/kg. Those values are compatible with the natural *background* evaluated for neapolitan soils by Cicchella et al. (2005) and for salernitan soils by De Vivo et al. (2008). Higher values can be found in the inner Appennine belt (32-56 mg/kg), in the southern area (56-64 mg/kg), and in the Solofra basin, which concentrations have already been explained with an anthropic contribute (Albanese et al., 2012 e 2015; Adamo et al., 2015).

Only 0.8% of the analyzed samples exceed the CSC threshold value for residential/public use (150 mg/kg). Those samples are concentrated in Agro-Nocerino-Sarnese area, and in the Solofra basin (Siano, Bracigliano, Mercato San Severino), where is located the soil which Cr concentration overpass the CSC for industrial/commercial use as well (800 mg/kg).

1.7.6 Copper (Cu)

1.7.6.1 Properties, applications and effects on human health

Copper (Cu, atomic number 29) is a calcophile transitional metal. It can occur in his metallic form (native copper), or form sulphides, like chalcopyrite $CuFeS_2$, or oxides, but usually is dispersed as trace element in some minerals, such as biotite, pyroxene, amphibole; so the contents of lead are greater in basalts and gabbro (40-60 ppm) and ultramafic rocks (40 ppm) than in intermediate (ca. 20 ppm) or granitic rocks (ca. 12 ppm) (Wedepohl 1978). Copper is strongly concentrated in hydrothermal mineralization and it is possible to find it in association with Ag and Au or with Pb, Zn, Mo, As, Se and Ni in sulphide deposits, so it is used in geochemical prospecting as a pathfinder for copper mineralization and many types of gold deposits.

In the surface environment, Copper is mobile under oxidizing, acidic conditions, with pH values between 5 and 6 and the affinity with organic matter is high, so it is bounded by Fe and Mn oxides and by clay minerals. In non-mineralized sediments, Cu concentrations are mainly determined by mafic detritus, secondary Fe and Mn oxides, clay minerals and organic matter (Forbes et al., 1976). Fine-grained clastic rocks, particularly black shale, are

typically enriched in Cu (ca. 50 ppm) relative to quartzo-feldspathic and carbonate sediments (5–15 ppm).

Average Cu contents in soils varies from 13 to 24 mg/kg. Copper normally accumulates in the surface horizons, a phenomenon explained by the bioaccumulation of the metal and recent anthropogenic sources (Kabata-Pendias 2001).

Copper is used in building construction (roofing, plumbing), electric and electronic products, power generation and transmission, industrial machinery, and car manufacture. Other anthropogenic sources of Cu in the environment are, apart from the industrial, mining and smelting activities, its uses in agriculture as a fungicide and herbicide, especially in viniculture, and as a wood preservative.

Copper is an essential trace element for all organisms, and humans can tolerate levels up to 12 mg per day (WHO 1996), although the element can be toxic at extremely high levels.

1.7.6.2 Cu distribution in top soils of Campania region

The concentrations in the analyzed top soil samples are between 2.5 and 2395 mg/kg, with a median value of 63 mg/kg. This concentration range is higher than the Cu contents measured in the Italian (3-215 mg/kg, median of 22 mg/kg, De Vivo et al., 2008a) and European top soils (0.81 - 256 mg/kg, median value of 12 mg/kg, De Vos et al., 2006).

The dot map distribution shows that the highest values, >316 mg/kg are centered in the Vesuvian - Neapolitan area (up to Phlegrean area and Ischia) and in the Avellino-agro Nocerino area, up to the municipalities of Solofrana basin (Siano, Bracigliano, Castel San Giorgio, Mercato San Severino). Regionally, 30% of the samples show high values, above 120 mg/kg, locally, especially around the Vesuvio, the values reach 600 mg/kg. These high values are localized only around the the vesuvian, neapolitan and phlegrean areas, being clearly related to the volcanic sediments and to the hydrothermal activity.

The interpolated map shows that the highest Cu concentrations are distributed around the vesuvian (242-2356 mg/kg) and phlegrean municipalities (123-599 mg/kg). Another area with high Cu values (123 - 599 mg/kg) is located in the Agro Nocerino Sarnese, in particular in the area included between Avellino and Salerno provinces, the Solofra basin, where the industrial and agricultural activities are widely diffuse.

The baseline map confirms the previously exposed trend, showing the highest concentration values in the vesuvian area (571 - 836 mg/kg), controlled by the volcanic origin of soils and by the secondary volcanic activity. Here these high concentrations can be related as well to the agricultural activities taking place on the slopes of the volcano. The same origin of the high concentration there is probably in the Solofra basin and in the Agro Nocerino Sarnese area (154 - 571 mg/kg). Here there is not only the influence of the products used in agriculture, but also the contributes due to the presence in the territory of 160 tanning plants. The surrounding area shows values between 42 and 154 mg/kg,

probably influenced by agricultural activities. The remaining inner territory, together with the Cilento area, is characterized by the lowest values, below 42 mg/kg. Copper reveals an overcoming of the intervention limits (CSC), established by the law D.L. 152/06, for the residential use (30% of the analyzed samples) and for industrial use top soils (2.4 % of the analyzed samples). All the neapolitan metropolitan area, from the Phlegrean area to the Agro Nocerino Sarnese and Avellino and Salerno areas, has top soils concentrations above 120 mg/kg (residential use). The overcoming in the top soils of the industrial use intervention limit is more restricted in the vesuvian municipalities, with some isolated values in Avellino, Salerno and Solofra basin.

1.7.7 Mercury (Hg)

1.7.7.1 Properties, applications and effects on human health

Mercury (Hg, atomic number 80) is a rare calcophil transition metal, although it's been considered a native metal for a very long time. The main mineral is cinnabar, HgS. Because of the large size of the Hg^{2+} ion, its incorporation into many rock forming silicate minerals is precluded. Granite have generally much higher Hg contents (average 80 µg/kg) than mafic igneous rocks, basalt and gabbro (typically 10 µg/kg). Much higher Hg levels (up to 1500 µg/kg) have been found in eclogite and peridotite in inclusions in kimberlite pipes, suggesting that the deep crust and upper mantle may be considerably enriched in Hg compared to the upper crustal rocks.

The main sources of Hg mineralization are found in volcanic hot springs and sedimentary rocks altered by phreatic activity, such as subduction zones.

In sedimentary rocks, the highest Hg levels are in shale (400 µg/kg), particularly in organic-rich black shale. In carbonate (40 µg/kg) and sandstone rocks (30 µg/kg) the Hg contents are lower (Wedepohl 1978). Coal shows very variable Hg levels and can reach very high levels (<1000 µg/kg).

The mobility of Hg in soil is highly dependent on its form and, in general, it has a strong tendency to bind to organic material. In the soil the Hg content varies between 20 and 150 µg/kg, and generally is not higher than 400 µg/kg (Kabata-Pendias, 2001); it is controlled by the presence of organic matter and S in the soil.

Most mercury is derived from natural sources, although Hg concentrations in the environment are increasing as a result of human activity. Mercury is the only metal existing in liquid phase at room temperature, and for its high density and physical properties, it finds wide use in thermometers and barometers. It finds also application in chemical and electrical industries (e.g. mercury-vapour lamps, advertising signs, mercury switches, batteries).

Mercury is non-essential and highly toxic to most forms of life. Metallic Hg is relatively inert and not readily taken up by organisms, but it is volatile and its vapour is toxic. The ability of micro-organisms to methylate Hg and its salts to create fat-soluble species, such as methylmercury (CH_3Hg^+) a strong tendency to build-up in the food chain. The compounds are readily taken up by aquatic organisms, and may be concentrated by higher members in the food web, such as fish and shellfish. The main exposure routes are ingestion of food and inhalation, especially for its use in paints, waxes, furniture polish, softeners, filters for air conditioners. Chronic exposure to dietary methylmercury and Hg vapour leads to the typical neurotoxic symptoms associated with Hg

poisoning, including disruption of the nervous system, damage to brain functions, DNA and

chromosomal damage and negative reproductive effects, such as sperm damage, birth defects and miscarriages.

1.7.7.2 Hg distribution in top soils of Campania region

The Hg concentrations in the analyzed top soil samples are between <5.0 and 6775 µg/kg, with a median value of 58 µg/kg. This concentration range in Campania region is higher than the Hg contents measured in the Italian (9 - 1350 µg/kg, median of 60 µg/kg, De Vivo et al., 2008a) and European top soils (9 - 1350 µg/kg, median value of 37 µg/kg, De Vos et al., 2006).

From the dot distribution map is it possible to observe that 95% of the campanian top soils has concentrations <320 µg/kg, being in the range considered normal (<400 µg/kg) by Kabata-Pendias (2001). The 4% of the samples (95° percentile) has Hg concentrations higher than 320 µg/kg, and the 1% is higher than 1000 µg/kg. Those samples are mainly localized in the metropolitan area of Naples, and in a small part in Salerno, Caserta, Avellino and Benevento cities, in Sorrento peninsula, Agro-Nocerino-Sarnese area and Sele mouth.

The interpolated map displays the majority of the region having low Hg contents (<147 µg/kg); furthermore, it shows that in some inner areas of Appennine belt and Cilento coastline Hg is even lower than 58 µg/kg. The higher Hg concentrations can be found exclusively in the Neapolitan area, and in some small areas in Aversa, Sorrento, and Sele mouth.

The *background/baseline* map shows a clear geolithologic control at regional level on the values lower than 138 µg/kg. The soils with concentrations ranging between 138 and 406 µg/kg can be found in the province of Naples, Agro-Aversano area, Sele mouth, Vallo di Diano, reflect the anthropic contribute that can be found in these areas.

The CSC map confirms this distribution. The 1% of the samples that overcomes the CSC threshold values for residential/public use (1000 µg/kg) is concentrated in the metropolitan area of Napoli, Sorrento peninsula, Benevento, Caserta. Only the concentration of one sample overcomes the threshold for industrial/commercial use (5000 µg/kg) in Acerra city.

1.7.8 Nickel (Ni)

1.7.8.1 Properties, applications and effects on human health

Nickel (Ni, atomic number 28) is a siderophile metallic element with chalcophilic and lithophilic affinities. It forms several minerals, and can substitute Fe^{2+} during fractionation, being partitioned into ferromagnesian minerals, such as olivine, ortopyroxene and spinel. The abundance of Ni in igneous rocks generally correlates with those of Mg, Cr and Co. For its calcophile properties it can be found in appreciable amounts in sulphide minerals, in association with Co, Cu and Pt.

In sedimentary rocks, Ni is mostly held in detrital ferromagnesian silicate minerals, detrital primary Fe oxides, hydrous Fe and Mn oxides, and clay minerals. It is more concentrated in shale (up to 90 mg/kg) than in greywacke (ca. 40 mg/kg), quartzitic sandstone (ca. 20 mg/kg) and limestone (<5 mg/kg).

Nickel mobility is generally restricted by its tendency to be sorbed by clay minerals or hydrous oxides of Fe and Mn. In soil, the range of Ni values vary from 0.2 to 450 mg/kg and is strongly related to Mn and Fe oxides, especially in surface soil horizons, where it occurs mainly in organically bound forms (Kabata-Pendias 2001).

Anthropogenic sources of nickel include fertilisers, steel works, metal plating and coinage, fuel combustion and detergents (Reimann and de Caritat 1998). Monel is a metal alloy composed by Ni and Cu that is resistant to seawater corrosion, making it ideal for boat propellers and desalination plants. When mixed with some organic complexing agents, Ni is capable of forming neutral or negatively charged complexes, making the metal highly mobile in relation to other trace elements. Consequently, Ni concentrations may be high in stream water contaminated by sewage and leachate from waste tips.

Nickel can be assimilated by human organisms through air, food and water. Some foods, such as chocolate or fat foods contain high levels of Ni. The exposure to low content of Ni can cause breathing problems and allergic reactions. Ni and his compounds are part of the Carcinogenic Group listed by IARC.

1.7.8.2 Ni distribution in top soils of Campania region

The Ni concentrations in the analyzed top soil samples vary between 0.5 and 101 mg/kg, with a median value of 14.7 mg/kg, much lower than the Ni contents measured in the Italian (2.73 - 2690 mg/kg, median of 33 mg/kg, De Vivo et al., 2008a), and more similar to the European top soils, despite the highest maximum values (2 - 2690 mg/kg, median value of 14 mg/kg, De Vos et al., 2006).

The dot distribution map shows that 90% of the sampled sites has Ni concentration < 32 mg/kg; the soils of the Campanian plain and volcanic areas have Ni contents < 22 mg/kg, with the lowest concentrations in the Phlegrean area. The 5% of the sites with concentrations > 50 mg/kg (95° percentile) is located in the Appennine areas of Benevento, Avellino and Salerno provinces, characterized by flysh and silico-clastic lithologies, with clay levels. Some sample with high concentration can be also found in the urban areas of Napoli and Salerno, and in the Sorrento peninsula.

In the interpolated map is better evidenced the lithologic control on the Ni distribution, in particular on the high concentrations that can be found in Benevento province, where the clay soils leads to Ni concentrations >28 mg/kg. Other high values (up to 54 mg/kg) can be found in soils developed on sedimentary and calcareous units, such as the Vallo di Diano, Alburni Mountains, Pennarone Mounts, up to the southern coastal areas (Ascea, Sapri). Here Ni tends to accumulate in alcaline soil, due to its tendency to be absorbed by clay minerals and Fe-Mn hydroxides. Contrary the volcanic soils shows Ni contents >28 mg/kg, and <14 mg/kg in the Phlegrean area.

The *background/baseline* map shows Ni concentrations in a range between 14-37 mg/kg in the majority of the regional territory. The higher background values (53-59 mg/kg) can be observed in a small area in the north of Benevento city, and in Vallo di Diano area.

The Ni concentrations does not show an overcoming of the CSC threshold values for residential/public use (120 mg/kg) and industrial/commercial use (500 mg/kg).

1.7.9 Lead (Pb)

1.7.9.1 Properties, applications and effects on human health

Lead (Pb, atomic number 82) is a calcophile metallic element, the most abundant among the transition metal elements. It forms several important minerals, such as galena, anglesite and cerrusite, but, for the similarity in size of Pb^{2+} ion with K^{+} and Ca^{2+}, it replaces these ions, so it is widely dispersed as trace elements in several minerals, such as k-feldespar, plagioclase, mica, zircon and magnetite. This is confirmed by enrichments in felsic igneous rocks (granitic values: 15-19 mg/kg, syenite: 12 mg/kg) and in crust (13 mg/kg), than in mafic rocks (ultramafic: 1 mg/kg; basaltic: 6 mg/kg). Lead is mobile during the late stage of magmatic processes and we can find it in association with Ag or as sulphide with Cu, Zn, Fe and Sb in hydrothermal mineralization. So it is used as pathfinder for Sedex and VHMS deposits, and for gold.

The mobility of Pb is usually low, because of the tendency of being absorbed by Fe and Mn oxides and by organic matter. In area of sulphide mineralization, Pb is mobilized by acidity derived from the weathering of galena and other sulphide minerals. The contents of both the above mentioned primary detrital minerals, clay minerals and organic matter, controls the distribution of Pb in sedimentary rocks. Pure limestone (ca. 5 mg/kg) and

quartzitic sandstone (ca.10 mg/kg) are typically depleted relative to shale and greywacke (ca. 23 mg/kg). The sedimentary rocks with the highest concentrations are the black shales.

In soils as well, the natural Pb content is related, not only to the parent rock, but also to the type of soil. Soil of clay minerals, Mn oxides, Fe and Al hydroxides and organic matter are enriched in Pb (Kabata-Pendias 2001).

Lead has a large use in industries (metal alloys for welding, pottery glazes, batteries, old paints, tv and pc glasses). The hazard in industrialized countries is due to the emissions in the atmosphere of tetraethyl Pb due to the combustion of fuels, although unleaded petrols, that can reduce the levels of Pb in road dusts, have been introduced. Metallic detritus in metalliferous mining, especially sulphide ores, can be another source of contamination.

Lead is one of the four metals with the worst effects on the human health and it has no known biological role in plants or animals; his compounds are toxic for inhalation and ingestion. It can be diffused through the food chain (in fruits, vegetables, meat, sea fruits, wine) and potable water, causing mental impairment in young children, neuropathy and hypertension in adults and may be lethal at high levels, e.g., over 25 μg/kg of body weight (WHO 1996).

1.7.9.2 Pb distribution in top soils of Campania region

In the analyzed top soil samples, the contents of Pb are between 3.1 and 2053 mg/kg, with a median value of 54 mg/kg, significantly above the measured values in the superficial soils of Europe (range: 5.3 - 970 mg/kg, median: 15 mg/kg) (De Vos et al., 2006) and Italy (range 2.55 - 204 mg/kg, median: 32 mg/kg) (De Vivo et al., 2008a).

In the dot map (Fig. 1.8a), the highest values are in correspondence of the most anthropic areas with intensive vehicular traffic. All the urban areas, from the coastline Domizio-flegreo to Agro-Aversano and the Solofra basin up to Avellino and Salerno, that comprehend 15% of the samples, have values above 100 mg/kg. Among these, the samples with contents above 250 mg/kg, locally exceeding 1000 mg/kg, are localized in the metropolitan city of Naples and Salerno, and along the coastline Domizio, near Castelvolturno, with some spotted values in Benevento and Caserta as well.

In the interpolated map (Fig. 1.8b), the more extended areas with values above 1000 mg/kg are around the city of Naples, Salerno, Castel Volturno (river mouth of the Sele), and in a small area in south of Avellino (Solofra basin), where the maximum values are reached. The internal areas have the lowest concentrations, under 42 mg/kg, reaching the minimum (under 23 mg/kg) along the Apennine reliefs.

The baseline distribution map (Fig. 1.9a) confirms the anthropogenic influence on the top soils of the Campania coastline, with values higher than 65 mg/kg in the more urbanized areas from Castel Volturno, to Caserta and Avellino, and the highest values (> 111 mg/kg) in correspondence of the main urban centers (Napoli, Salerno) and the Solofra basin. The

southern part of the region, together with the internal areas (provinces of Benevento, Caserta and Avellino) have low values, compatible with the geolitogenic characteristics of these zones.

In the maps of the CSC intervention limits (Fig. 1.9b), we can see that 15% of the analyzed samples exceeds the CSC limit for residential use, while 0.2% of the samples is above the CSC limit for the soils destined to industrial/commercial use. These top soils with Pb values exceeding the intervention limits are localized in the most anthropic areas of the region, from the Domizio-Phlaegrea coastline, to Salerno, especially in the Neapolitan province and the main urban centers (Avellino, Caserta and Salerno). According to previous works (Cicchella et al., 2005), the high concentrations in the urban areas (especially in the neapolitan area where the measured contents are above 100 mg/kg) are due to the lead-base fuels used until '90, and, because of the characteristic of lead to being persistent, the soils in these areas will keep high concentrations until a new reclamation.

1.7.10 Antimony (Sb)

1.7.10.1 Properties, applications and effects on human health

Antimony (Sb, atomic number 51) is a low abundance calcophile trace element. It forms several rare minerals, such as stibnite, valentinite, but it is usually present at trace levels in minerals such as ilmenite, and olivine, where it can substitute Fe. The highest concentrations (>3 mg kg-1) typically occur in the vicinity of hydrothermal deposits of galena and sphalerite. Fine-grained argillaceous and organic-rich sediments are typically enriched in Sb (>1 mg/kg) relative to their parent igneous lithologies, reflecting the strong tendency for the element to become sorbed to hydrous oxides, organic residues and clay minerals in favourable environments.

In stream sediment, Sb life is controlled by the detrital sulphide minerals in which it is contained, e.g., stibnite, sphalerite and galena some of which may weather relatively rapidly under acid, oxidising conditions. Further remobilisation of Sb in the surface environment (pH 4.0-8.0) is rather limited due to the tendency of Sb^{3+} to hydrolyse to insoluble basic salts and be absorbed by secondary hydrous oxides of Fe, Al and Mn. Antimony in the form of oxide is largely immobile (Wedephol, 1978).

In soil, Sb can be enriched in the A-surface horizon due chelation with organic matter, and in the B-horizon as a result of strong adsorption of Sb by hydrous Fe-oxides and clay minerals.

With its low natural abundance, Sb is a useful indicator of industrial contamination.

Antimony is used in the manufacture of lead solder, batteries, arms and tracer bullets, composite car body panels and dashboards. Anthropogenic Sb is associated with metalliferous mining (gold and sulphides) and metal smelting. It is also associated with coal

combustion, urban waste and car exhaust fumes, as well as flame proofing compounds, paints, ceramic enamels, glass and pottery.

Antimony is one of the toxic metals diffused in working spaces. It causes intoxications if contained in inhaled dust. High concentrations of Sb are highly toxic – more so than either arsenic or lead – and Sb is a known carcinogen.

1.7.10.2 Sb distribution in top soils of Campania region

The Sb concentrations in the analysed top soil samples vary between <0.02 and 43 mg/kg, with a median value of 0.66 mg/kg. Antimony concentrations in top soils of Campania region are higher than the Cu contents measured in the European top soils (0.02 - 31.1 mg/kg, median value of 0.60 mg/kg, De Vos et al., 2006), while the Italian ones are much lower (0.13-4.26 mg/kg, median of 0.71 mg/kg, De Vivo et al., 2008a), also if comparable in the median value.

In the dot map it possible to prove that 95% of the sampled sites have Sb concentrations < 3 mg/kg, similar to the italian values; 5% of the samples have concentration >3 mg/kg, 4,2% have concentrations between 3 and 10 mg/k, 0,7% between 10 and 30 mg/kg, and just three samples (0.1%) have concentrations between 30 and 43 mg/kg. The sites with Sb concentrations >3 mg/kg correspond to the areas with high anthropic impact, such as the urban areas of Napoli and Salerno, the Agro-Nocerino-Sarnese (Solofra basin) and Domitio-Aversana areas, and Vallo di Diano.

The interpolated map evidences the difference among the urban areas, with the highest values (>1.6 mg/kg), limited to small areas, and the remaining Campania region, characterized by Sb concentrations <0.8 mg/kg.

The background/baseline map shows two areas; one including the Appennine belt and part of Cilento, with values <0.5 mg/kg; one along the coastline with higher values (Sb > 1.5 mg/kg), including the areas with high anthropic impact (Napoli, Salerno, Solofra basin, Domitian coastline).

Only 0.3% of the samples show an overcoming of the CSC threshold values for residential/public use (10 mg/kg), while just three samples overcome the threshold values for industrial/commercial use (30 mg/kg), limited to the already mentioned urban areas with high antrhopic impact.

1.7.11 Selenium (Se)

1.7.11.1 Properties, applications and effects on human health

Selenium (Se, atomic number 34) is a chalcophile non-metallic element forming several rare minerals, but is more widely presents as an accessory element replacing S, that has a

similar geochemistry, in more common sulphide minerals, such as pyrite, chalcopyrite, pyrrhotite and sphalerite. Its concentrations in volcanic rocks are generally low, because during volcanic activity, Se tends to escape subjected to high temperature volcanic gases. Due to similarities in the chemistry of Se and S, Se is a chalcophile element and is concentrated in sulphide ore deposits, uranium deposits in sandstone and the diagenetic pyrite of fine-grained sediments. Organic-rich sediments (black shales) and phosphate rocks are enriched in Se.

Selenium is immobile under reducing conditions, and highly mobile under oxidising (acidic, neutral and alkaline) conditions. It can be sorbed by clay minerals and Fe hydroxides. The behaviour of Se in highly calcareous soil is of special concern, because Se becomes easily water soluble when soil is low in sesquioxides. Another significant observation is the adsorption of Se by clay minerals, which decreases with increasing pH values and becomes negligible above pH 8 (Kabata-Pendias 2001).

The glass and ceramics industry are the largest users of Se. It is also used in the electronic industries, due to its photovoltaic properties. In industrial areas, the burning of fossil fuels,

e.g., combustion of coal in electricity generation, leads to an increase of Se in the environment from atmospheric deposition. Other sources of Se include smelters, wastewater and some phosphate fertilisers.

Selenium is a biologically active element and is essential in the diet of many organisms (30-40 μg/day, WHO, 1996), and grains, cereal and meat usually contain enough Se to provide the necessary daily requirement. However, the optimal dietary requirement for Se lies in a narrow range; the maximum limit for ingestion in adults is 200 μg/day (20 μg/day is the lower limit). One of the main exposure ways is the food itself, that can contain higher levels, because of the use in arable lands of fertilizers rich in Se. Selenium can be toxic at higher levels, causing hair and nail loss, skin disorders, nerve damage and abdominal cramps. Selenium poisoning may become so severe in some cases that it can even cause death.

1.7.11.2 Se distribution in top soils of Campania region

Selenium concentrations vary between <0.1 and 2.4 mg/kg, with a median value of 0.4 mg/kg. There are no available data for Se concentrations in italian and european top soils. In Campania region some data was already available in the urban areas of Napoli, Avellino, Benevento, Caserta and Salerno, Domitio-Phlegrean coastline, and Agro-Aversano area, and the concentrations are comparable with the regional database.

The dot distribution map shows quite low Se concentrations, with 97.5% of the samples <1 mg/kg. The higher values, between 1 - 2.4 mg/kg, can be found in some spots, not

showing clear distribution patterns, a part the Domitian coastline, close to the Volturno river mouth.

The interpolated map confirms the previous observations, with generally low values (Se < 1 mg/kg), and some high values (1 - 2.4 mg/kg) in limited areas in Benevento and Salerno provinces (Morcone and Caselle in Pittari), and close to Castelvolturno city.

The *background/baseline* map shows Se concentrations compatible with the natural background values evaluated by Cicchella et al. (2005) (0.2 - 1.1 mg/kg).

Selenium concentrations are always lower than the CSC threshold values established by the D.Lgs 152/06 for residential/public use (3 mg/kg) and industrial/commercial use (15 mg/kg). Wide areas have Se concentrations quite low (<0.2 mg/kg), close to the limit value indicated by Tan et al. (2002) for soils destined to agricultural activities, because Se is an essential nutrient for human organism, and a deficiency of this element can cause serious damage in the resident population.

1.7.12 Tin (Sn)

1.7.12.1 Properties, applications and effects on human health

Tin (Sn, atomic number 50) is a relatively rare, siderophile metallic element. It forms several minerals, including cassiterite, and is present as an accessory element in minerals, such as biotite, muscovite, amphibole, sphene and rutile, thanks to the ability of Sn^{4+} to replace Ti^{4+} and Fe^{3+}. The small ionic radius and the high charge of Sn^{4+} ion let it strongly concentrate in residual melts, and thus it becomes enriched in felsic relative to mafic igneous rocks. Economic levels of Sn can be found in evolved granite, often containing casserite as disseminated accessory phase, in dhydrothermal veins and metasomatic deposits closely associated with highly siliceous lithologies (Ure and Berrow, 1982). In sedimentary rocks, the concentration of Sn is primarily determined by the abundance of resistant minerals such as cassiterite, sphene and magnetite. Small amounts of Sn dissolved during the weathering of mica may precipitate with Al rich hydrolysates; this would explain the widespread accumulation of the metal in bauxite. Argillaceous and calcareous sediments typically contain Sn at levels in excess of the crustal average (4–6 mg/kg), while sandstone (ca. 1 mg/kg) are generally depleted. In tropical soil, values of up to 60 mg/kg Sn have been recorded, with a large proportion held in clay and in organic matter (Aubert and Pinta, 1977).

In stream sediment, most detrital Sn is held in resistant phases, such as cassiterite, which

release Sn very slowly during weathering. Inversely, Sn contamination can derive from ferrous wastes, rapidly leached and mobilized. Also the human-made organo-tin pesticide are weathered faster than cassiterite. In areas where Sn mineralisation is absent, Sn is an excellent indicator of contamination. Contaminated samples are often indicated by the presence of high levels of other metals such as Pb, Zn and As, which are not associated with

Sn mineralisation. Weathering of most natural and anthropogenic Sn carriers is intensified under acid, reducing conditions. Any Sn^{2+} released oxidises rapidly and is subsequently bound to secondary oxides of Fe or Al as $Sn(OH)_4$ or $Sn(OH)_3O^-$.

Tin has been used since 3000 BC (alloyed with Cu to form bronze and with Cu, Sb and Pb to form pewter). Nowdays, its main applications are in solder, Sn plating, and in chemicals. It is also used as a stabiliser in plastic production. Anthropogenic sources of tin include coal and wood combustion, waste incineration and sewage sludge, agricultural pesticides and wood preservatives.

Organo-tin compounds are persistent and not easily biodegradable, being the most dangerous form of Sn for humans. An example is the well documented cases of shell abnormalities in shellfish and imposed in gastropods caused by tributyltin in anti-fouling paints for ships. Toxic levels of inorganic Sn can cause growth depression and anaemia in humans, and also interferes with the metabolism of Zn, Cu and Ca.

1.7.12.2 Sn distribution in top soils of Campania region

Tin concentrations in the analyzed soils varies from 0.2 and 126 mg/kg, with a median value of 3.3 mg/kg. Those values in Campania soils are higher than the concentrations in European (maximum value 106 mg/kg, median value 3 mg/kg) (De Vos et al., 2006) and Italian top soils (1-19 mg/kg, median value 4 mg/kg) (De Vivo et al., 2008a).

The dot distribution map shows high Sn concentrations (>10 mg/kg) in the metropolitan area of Napoli, especially in the north-western sector and in the Phlegrean area, Salerno, and Agro-Nocerino-Sarnese area. The Domitian coastline and Agro-Aversano areas have lower concentrations, between 3-10 mg/kg. The remaining territory have Sn concentrations < 3 mg/kg.

The interpolated map confirms that most of the region have Sn concentrations < 4 mg/kg, with wide areas in the eastern part of the Appennine belt and in Cilento area where they decrease still more (< 1 mg/kg). Higher concentrations (4-11 mg/kg) can be found along the urban areas of the Domitian coastline (Sessa Aurunca up to Battipaglia). Highest *hot spots* (> 20mg/kg) are present in the Domitian coastline, in some municipality to the NW of Napoli, in Agro-Nocerino-Sarnese area and Salerno city.

In the *background/baseline* map high contents (4-9 mg/kg) are distributed along the coastline, from Cilento to Domitian area, and Vallo di Diano. The geolithologic control is valid, due to the development of soils on volcanic rocks, but the anthropic contribute (illegal spills) cannot be excluded, especially in the Caserta province (Mt. Maggiore and Mt.Taburno), where can be found the highest Sn values.

Almost all the sampled sites show an overcoming of the CSC threshold values established by the D.Lgs. 152/06 for residential/public sites (1 mg/kg), while there are no overruns of the threshold for industrial/commercial use. Is evident that the CSC for

residential/public use is not appropriate and should be modified with a major attention to the natural background.

1.7.13 Thallium (Tl)

1.7.13.1 Properties, applications and effects on human health

Thallium (Tl, atomic number 81) has both calcophile and litophile properties. Thallium minerals are very rare and are formed exclusively during the epithermal stage of hydrothermal activity or under supergene conditions. Host minerals that provide a major source of Tl in igneous and magmatic rocks include plagioclase, K-feldspar, biotite, and mica minerals such as phlogopite and muscovite. In nature it is possible to find it in association with Nb and Li in pegmatite. The distribution of Tl in the Earth's crust shows that its concentration appears to increase from ultramafic to felsic rocks, and with increasing clay content of sedimentary rocks. Calcareous sedimentary rocks contain the least thallium. Thallium ion Tl^+ is usually associated with K and Rb, because of its similar geochemical properties with K (Wedephol, 1995). During weathering, Tl is readily mobilised and transported together with alkaline metals, but is most often fixed by Mn and Fe oxides and organic matter.

Thallium is used in the electronics industry, glass manufacturing, for a variety of alloys, in the pharmaceutical industry, and as a rat poison and ant killer. Thallium can be emitted to the environment via coal combustion, waste incineration, petroleum refining, and from Pb, Zn and Cu smelters. Thallium is also used in pesticides, although this has been banned in many industrialised countries.

Thallium is extremely toxic, but little studied, because is naturally present in small amounts. It can be easily assumed through skin and respiratory and intestinal tracts (Fowler, 1982). Thallium poisoning affects the central nervous system, causing visual disorders, such as failing eyesight or total blindness, hair loss and ultimately death.

1.7.13.2 Tl distribution in top soils of Campania region

Thallium concentrations in the analyzed samples varies from 0.05 and 69 mg/kg, with a median value of 1.33 mg/kg. Those contents are higher than the European (0.05 - 24 mg/kg, median value 0.66 mg/kg) (De Vos et al., 2006) and Italian top soil contents (0.05 - 6.08 mg/kg, median value 0.75 mg/kg) (De Vivo et al., 2008a).

From the dot distribution map is it possible to observe that most of the region has values < 3 mg/kg (97.5% of the sampled sites). Intermediate values between 2.5 and 3 mg/kg (7.5% fo the sampled sites) are located in the vesuvian area, up to Mt. Taburno and Caserta province; other areas are around Roccamonfina volcan, from the coast to the Matese

mountains, and in the Agro-Nocerino-Sarnese area (Solofra basin). The remaining 2.5% of the samples with Tl concentrations > 3 mg/kg can be found in the Vesuvian area up to Nola, in the southern part of Roccamonfina, Sessa Aurunca, and in Ischia island, with peaks of 69 mg/kg.

The interpolated map shows two distribution *patterns*; the first one with values > 1.6 mg/kg in volcanic areas (Vesuvian area, up to Caserta and Avellino provinces, Ischia, Agro-Aversano, Roccamonfina); the second one in those areas with silico-clastic lithologies, that lead to Tl concentrations < 1 mg/kg.

The *background/baseline* map emphasizes that the lower values, < 0.5 mg/kg, are characteristic of the silico-clastic deposits in the eastern Apennine belt and Cilento area. Going to the W, the Tl contents grow from 0.5-1.6 in the closest part of the Appennine (from Alife to Sapri), to the highest values >1.6 mg/kg in volcanic soils of vesuvian area and Phlegrean fields. Those latter are in line with the background values proposed by Cicchella et al. (2005) for vesuvian (2.7 mg/kg) and phlegrean (1.7 mg/kg) areas. The geolithologic control prevails for Tl distribution in the Campania soils.

The CSC threshold value for residential/public use (1 mg/kg) is exceeded in wide areas of Campania region, and in some sites on Ischia island this happens also the CSC for industrial/commercial use (10 mg/kg). Those overcoming are clearly diffused in volcanic areas, so probably due to the lithogenic origin of the soils. The Tl threshold values should be renewed, basing on the knowledge of the natural background values.

1.7.14 Vanadium (V)

1.7.14.1 Properties, applications and effects on human health

Vanadium (V, atomic number 23) is a lithophile metallic element at low pressure, but may be siderophile at the elevated pressures. It forms several minerals (vanadinite, carnotite), and can be found as trace element in mica, apatite, pyroxene and amphibole. The trivalent ion V^{3+} has a similar ionic radius to that of Fe^{3+} (65 pm). Hence, V is frequently found as a substitute for Fe in magnetite and in the ferromagnesian silicate minerals formed during primary magmatic processes. Mafic rocks are typically enriched in V relative to most intermediate and felsic rocks. In ultramafic rocks, the V content generally reflects the abundance of minerals, such as Fe-TiCr oxides and pyroxene (Snyder, 1999).

The V content of sedimentary rocks reflects primarily the abundance of detrital Fe oxides, clay minerals, hydrous oxides of Fe and Mn, and organic matter. The average V

content of quartzitic sandstone and pure carbonate sediments is low (<15 mg/kg), with higher values in greywacke (40-150 mg/kg), shale (90-260 mg/kg), and clay (ca. 200 mg/kg) and particularly black shale.

The solubility of V in the surface environment is strongly controlled by its oxidation state: it is highly soluble in oxic environments, as V^{5+} although the presence of U and

phosphates can result in the formation of highly insoluble complexes. Under more reducing conditions, the relatively immobile V^{3+} state dominates. In soil V will sorb to Fe- and Mn-oxides, clay and organic matter.

Burning of fossil fuels is the prime source of anthropogenic V emissions into the atmosphere. Vanadium is present in steel slag and in flue ash from heavy oil combustion, and is also used in special steel alloys and as a catalyst in industrial chemistry. Regarding V in agricultural soil, it is important to note that high values of V were reported in some fertilizers.

Vanadium is biologically active and is an essential nutrient for many animals. Its intake comes primarily from some foods, such as eggs, apples, buckwheat soy, olive and sunflower oil. Vanadium compounds are not considered very toxic, although some workers that have been exposed to V dust, showed irritation of eyes, throat and nose. Vanadium toxicity depends a lot from his oxidation state; V^{5+} is the most toxic form. In severe cases, toxic levels of V causes the inhibition of certain enzymes with animals, which has several neurological effects, and can cause breathing disorders, paralyses and negative effects on the liver and kidneys.

1.7.14.2 V distribution in top soils of Campania region

Vanadium concentrations in Campania top soils vary between 5 and 224 mg/kg, with a median value of 60 mg/kg. Regional contents are slightly lower than the European (2.71-537 mg/kg, median value 60 mg/kg) (De Vos et al., 2006) and Italian top soils V concentrations (14-277 mg/kg, median value 84 mg/kg).

The dot distribution map shows that most of the Campania top soils have V concentrations <110 mg/kg (85% of the sampled sites). The highest values are grouped in the vesuvian area, up to Nola and Vallo di Diano. Going far from the vesuvian areas, the V content decreases (<90 mg/kg), finally reaching the lowest values (<45 mg/kg) in the inner mountainous areas, along the Cilento coastline, and in the Phlegrean area.

From the interpolated map is it possible to identify three distribution *patterns* for V concentrations; the first one with low values (<50 mg/kg) in the eastern sector of the Apennine belt, and in Cilento area; the second one with intermediate values (50-90 mg/kg) in the central sector of the Apennine belt; the third one with high values (>90 mg/kg) in the vesuvian area, Solofra basin, close to Roccadaspide municipality, and in Vallo di Diano (between Mt. Cervati and Mt. Pennarone).

The *background/baseline* map shows a regional trend between 46 and 95 mg/kg. Lower V concentrations (<46 mg/kg) can be found in the Domitian, Phlegrean and Cilento coastlines, and in the Apennine areas. High values can be found close to Vesuvio (122-138 mg/kg) and on soils associated to volcanic lithologies (95-122 mg/kg). The same values are found in Vallo di Diano where, at contrary, cannot be identified geolithologic influences.

The 20% of the samples exceeds the CSC threshold values for residential/public use (90 mg/kg). There are not overcoming of the CSC for industrial/commercial use. The geo-lithologic contribute is evident for V contents in Campania soils, considering the natural *background* value of 120 mg/kg established by Cicchella et al. (2005). An anthropic contribute is instead evident for V concentrations >90 mg/kg in urban soils of Napoli, Avellino, Caserta, Salerno and Benevento, in soils of Domitian coastline, Solofra basin, Nola and Vallo di Diano.

1.7.15 Zinc (Zn)

1.7.15.1 Properties, applications and effects on human health

Zinc (Zn, atomic number 30) is a calcophile element, forming several minerals, like sphalerite, smithsonite and zincite, and is widely dispersed as trace element in some minerals, like pyroxene, amphibole, mica and magnetite. Zinc is compatible during the early stage of magmatic processes and has a similar ionic radii with Fe^{2+} and Mg^{2+}, so the substitution in some oxide and silicate mineral of these ions with Zn^{2+} is common. That's why Zinc and the enrichment of Zn is major in mafic than in felsic rocks (ultramafic 50 mg/kg; basaltic 105 mg/kg; granitic 39–60 mg/kg; syenite 130 mg/kg). It can be found in association with Cu, Pb, Ag, Sb, As in metal deposits.

The abundance in sedimentary rocks depends on the presence of ferromagnesian silicates, detrital oxides, e.g., magnetite, and clay minerals (Wedepohl 1978). Carbonate rocks (ca. 50 mg/kg) and quartzo-feldspathic sand (30-50 mg/kg) are generally depleted in Zn compared with greywacke (70-100 mg/kg) and shale (50-90 mg/kg). It has a great affinity with organic matter, so it has high values in oil shale.

Zinc mobility in the surface environment is greatest under oxidizing, acidic conditions; weathering of sulphide minerals in oxidizing conditions may give rise to high concentrations (>100 μg/l) of dissolved Zn sulphates and it is rapidly adsorbed to secondary oxides, clay minerals and organic matter.

The Zn content in soil depends on the nature of parent rocks, texture, organic matter and pH. Since Zn is easily absorbed by mineral and organic components in most soil types, it normally accumulates in the surface horizons (KabataPendias 2001).

Zinc mining, smelting and steel processing are the primary sources of Zn emissions to the atmosphere. Zinc is widely used as an anti-corrosion coating (galvanisation) of steel, in alloys (brass is an alloy of Cu and Zn), in solders, pipework, plumbing and water components, as a pigment in paint, in rubber products, in deodorants and in the manufacture of batteries. In the context of agricultural soil, Zn is used as a fertiliser and high concentrations of Zn can be observed in some phosphate fertilisers. Furthermore, Zn

compounds are also used in pig and chicken farming, and thus sewage sludge can contain high levels of the element.

Zinc is an essential trace element for humans, animals and higher plants. A recommended intake of 11.4 mg per day is suggested for adults (prasad, 1983). Excesses of Zn can cause health problems such as stomach cramps, skin irritations, vomiting, nausea and pancreas damage. The worst effects are due to deficiency, which symptoms include growth retardation, dermatitis and slow wound healing, defective immune system and, in extreme cases, birth defects.

1.7.15.2 Zn distribution in top soils of Campania region

The Zinc contents in the top soils of the analyzed area varies between 11.4 and 3210 mg/kg, with a median value of 91 mg/kg. The Zn concentrations in the Campania region are generally higher than the concentrations found in the other Italian top soils (37 – 396 mg/kg, median value of 81 mg/kg) (De Vivo et al., 2008a) and in European top soils (3 – 2900 mg/kg, median value off 48 mg/kg) (De Vos et al., 2006).

The dot map shows that high concentrations of Zn (> 240 mg/kg) are found in correspondence of the urban area that goes from the Phlegrean area to the Agro-Aversano area to the city of Salerno. In some single spots the concentration arrives up to 3210 mg/kg. In particular, the highest contents are diffusely located in the cities of Naples, Salerno and Caserta, and in some municipality of the Agro-Nocerino-Sarnese area.

The interpolated map better reveals the real distribution patterns of the Zn concentrations, showing that the highest contents, between 150 and 1217 mg/kg, are all along the city of Naples, Salerno, in the municipalities of the Solofrana basin and Agro Nocerino Sarnese, and, in a more restricted way, in the river mouth of the Volturno, in the Caserta province (W of Mt. Maggiore), in the Benevento province (between Morcone and San Marco) and in the Salerno province (Altavilla Silentina, Bellosguardo and Vallo di Diano). The coastline of Cilento and the internal areas of Apenine mountains have lower values (60-80 mg/kg, locally < 60 mg/kg).

The baseline map confirms that the highest concentration values (119 – 253 mg/kg) are localized in the urban areas, with a clear anthropogenic impact. The background values between 30 and 120 mg/kg, defined in Cicchella et al. 2005, are compatible with the baseline distribution here evaluated for the remaining Campania territory.

In the maps of the CSC intervention limits, 25% of the samples are above the intervention limit of 150 mg/kg for residential/recreational use. Only some localized samples are above 1500 mg/kg, the intervention limit for industrial/commercial use.

Chapter 2 – A regional approach to the environmental risk assessment - human health risk assessment case study in the Campania region

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2.1 Introduction

2.1.1. The environmental risk assessment

Environmental risk assessment is an issue widely diffused in the international scientific literature (Albanese et al. 2014) and extremely topical for preserving human health and natural ecosystems. The increasing anthropic impact on the environment moved the population and the political administrations to the conviction of needing a rehabilitation of the numerous contaminated sites in Italy and Europe, and carrying out activities for mitigate the pollution dispersion.

The geochemical cartography is fundamental for a correct management of the environment, because it can individuate the areas with anomalous contents of potentially toxic elements for humans end environment, circumscribe these areas, and plan intervention and restoration actions.

The main purpose of risk assessment is the probabilistic evaluation of damages on humans and environment coming in contact with one or more contaminated environmental media (soil, water, air, sediments, etc.). The general concept of environmental risk is expressed by the equation R = H * E (Ropeik and Grey, 2002), where H is the hazard generated by the presence in the environment of one or more potentially toxic substances; while E is the Exposure, expressing the effective possibility for humans to come in contact with the toxic substance released by the contaminated media. The exposure is dependent by some variables, such as: the contamination source type, toxicity, extension and distribution; the existence of pathways through which the contaminants can diffuse and migrate from the source to the receptor; the type of texture coming in contact with the contaminated media; the age of receptors; the frequency and duration of the exposure. The main exposure pathways for the human receptors are (Connor et al., 1998; Environ Italy, 2002; Provincia di Milano and URS Italia, 2008; Spence, and Walden, 2001):

- Food ingestion
- Drinking water ingestion
- Soil particulate ingestion
- Air particulate inhalation

- Dermal contact

Specifically, the equation leading to the determination of the dose, expressed as mg/kg/day, at which an individual is potentially exposed is estimated by the following general equation:

$$E = \frac{CR \times EF \times ED}{BW \times AT}$$

where:
E is the Exposure dose, expressed as mg/kg/day
CR is the Contact Rate or the amount of each contaminated medium swallowed, inhaled or contacted per time unit or event. It is expressed in m3/day for water and air, and in mg/day for soil;
EF is the Exposure Frequency, usually measured in days/year;
ED is the Exposure Duration, expressed in years;
BW is the Body Weight during the period of exposure, expressed in kg;
AT is the Average Time of exposure of an individual to a substance, expressed in days.

At the regional level, it is difficult to apply the classical methods of human health risk assessment used at the scale of a site (Demetriades, 2010; Tristán et al., 2000), due to the heterogeneity of lifestyles of the population, the variability of land use, and the relatively low amount of information on the distribution of inorganic and organic pollutants in the environmental media.

Some attempts for the regional environmental risk assessment have been made during the last years (Tristàn et al., 2000; Sorvari et al., 2007; Demetriades 2011; Pizzol et al., 2011; Zabeo et al., 2011; Albanese et al., 2014). In this PhD work a new methodology for assessing the human health risk, based on spatial analysis, is presented. An existing European-wide methodology for the preliminary assessment of human health risk at single contaminated sites (PRA.MS, EEA, 2004) is adapted to evaluate the risk at the regional level, by using geospatial analysis in GIS environment. The starting point is the systematic collection of topsoil samples in the Campania Region, an intensely populated and industrialized area in Southern Italy, and the determination of potentially hazardous elements.

2.1.2. State of the art of soil policies

Starting from the 1980's several incidents attracted the major mass media attention (e.g. Love Canal, New York State; Times Beach, Missouri; Lekkerkerk, The Netherlands) and motivated politicians to understand that pollution should be removed or contained completely (Ferguson, 1999). Some countries in Europe are pioneering in assessing

contaminated sites, such as the United Kingdom, Denmark, Germany, and especially The Netherlands, which developed an approach after the Lekkerkerk incident, and was used in many other countries. Other countries, such as France, Italy and Portugal, developed much later specific legislation for contaminated land and remediation (Ferguson, 1999). Of course, in this account the significant work on risk assessment of the United States Environmental Protection Agency should be mentioned (US EPA, 1989, 1991a, b, 1998a, b).

In May 1990 the European Environment Agency (EEA) was established by Council Regulation EEC 1210/90 and started its operations in Copenhagen in July 1994. The EEA's mission is to contribute to the improvement of the environment in Europe and to support sustainable development through the provision of relevant, reliable, targeted and timely information to policy-makers and the general public (EEA, 2004).

During the last years, some national environmental agencies developed in many industrialized countries ecological and human health risk assessment procedures for contaminated sites, widely implemented by legislation (APAT, 2008; DEFRA, 2011; Doe, 1995; Health Canada, 2010a, 2010b; USEPA, 1991, 2005, Albanese et al., 2014).

Several Technical Working Groups (TWGs), launched in 2003 in order to support the preparation of the Soil Thematic Strategy (STS) for the protection of soils, recommended that monitoring of soil should be limited only to identified potentially risk areas, as opposed to monitoring systems covering the entire territory. Focusing monitoring in selected areas would help to define priorities, increase efficiency of monitoring activities and reduce costs (EEA, 2004). The limited financial resources in most countries, is another factor that forces to reduce as much as possible the remediation strategies. Therefore, there is a strong need to develop, so called, relative risk assessment methodologies, which aim to identify and select the potential hazardous areas to be investigated more thoroughly or in order to prioritize the remediation actions (Pizzol et al., 2011).

In 2005, the EEA published a review of 27 existing and documented international methodologies for preliminary and simplified risk assessment of (potentially) contaminated sites, already in use in member countries and overseas at national or regional level for the prioritization and planning of soil remediation and protection programmes. All the reviewed methodologies adopt a qualitative (or semi-quantitative) approach to the assessment of site risks, describing risks in term of scores, rather than absolute estimates of health/ecological impacts (EEA, 2004). The scoring system is based on several parameters. The identification and listing of common parameters, used in the reviewed methodologies and their harmonization, helped in the selection of a set of parameters to be included in the proposal for a methodology for the identification of potentially hazardous areas for soil contamination in Europe. This methodology, called PRA.MS (Preliminary Risk Assessment Model for the identification and assessment of problem areas for Soil contamination in Europe; EEA, 2005a, b, 2006) is a tiered approach, that starts from a preliminary selection

of the sites, which are potentially hazardous, based on a source size criteria, and implementing it with fundamental risk elements, such as source hazard, pathways and receptor information (EEA, 2005a). Potentially hazardous areas are defined in the PRA.MS as areas where soil contamination is considered to pose significant risks to human health and/or ecosystems with impacts beyond the local environment (Quercia et al., 2006). The main sources of contamination are municipal and industrial waste disposals, mining sites, and industries.

2.1.3. Purpose of the research

The only drawback that the PRA.MS and the other 27 reviewed methodologies have is the absence of spatial analysis (Pizzol et al., 2011). The objective of this work is to implement the PRA.MS methodology, integrating the model of relative risk assessment for single contaminated sites, with spatial analysis procedures, developing a regional risk assessment methodology, which can be used by the regional administrations to select at regional level the potentially hazardous areas and to prioritize them. In order to support the spatial assessment of contaminated sites at the regional scale, as mentioned above, the most suitable tool is the Geographic Information Systems (GIS) (Pizzol et al., 2011). The GIS is the main tool to manage, manipulate, process, analyze, map, and spatially organize the data in order to facilitate the vulnerability analysis (Zabeo et al., 2011). Despite this, there are very few applications in risk or exposure assessment (Tristán et al., 2000 and references therein). The PRA.MS establishes both human health and ecological risk assessment procedures. However, since the Italian law (D.Lgs. 152/06) considers, only for soils, trigger and action limits (CSC) to assess the hazard for human health, we only carried out the human health risk assessment.

2.2 Risk assessment methods

2.2.1. Risk assessment using PRA.MS methodology

The general framework for the risk assessment adopted by the PRA.MS methodology (EEA, 2005b) is shown in Fig. 2.1 and it consists of several steps:

1) The exposure routes relevant for the human health risk are the following: Groundwater (GW), Surface water (SW), Air particulates (AIR), and Direct contact (DC);
2) For each exposure route, a Source-Pathway-Receptor model is assumed to assess the human health risk;

3) Representative parameters of the Source, Pathway and Receptor for the different exposure routes, are established by taking the common parameters of the existing methodologies and by their harmonization;
4) Parameters, alone or aggregated, represents factors;
5) The factors are given scores based on the qualitative or quantitative value of the parameters and have different weights depending on how well they describe the exposure routes indicators;
6) Factor scores are added up in order to aggregate each Source-Pathway-Receptor Indicator (as indicated in Fig. 2.1, there are 12 S-P-R Indicators);
7) S-P-R Indicators are multiplied for each of the exposure routes, to obtain the corresponding scores of the four exposure routes, and;
8) The overall risk is given a score by computing the root mean square of all exposure routes scores.

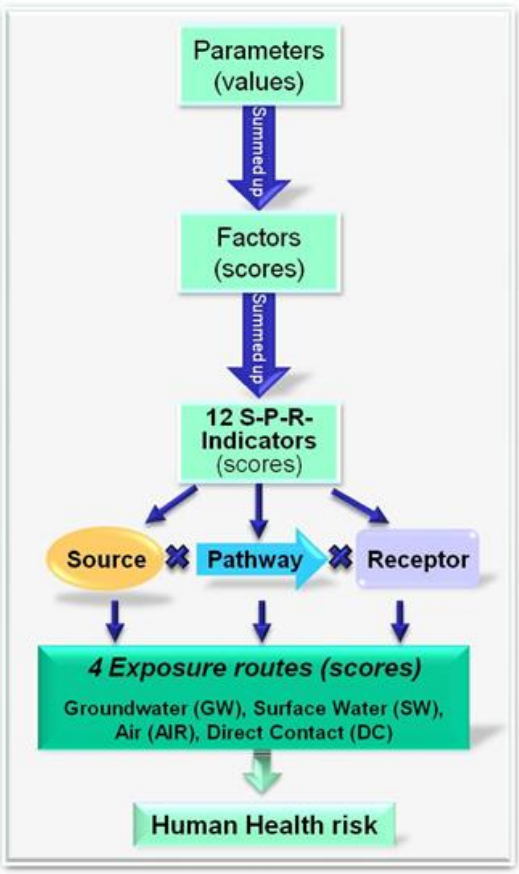


Fig. 2.1: *General framework of the PRA.MS methodology (modified after Quercia et. al., 2006).*

The PRA.MS methodology is a tiered approach, which starts from a pre-selection of the potentially contaminated sites (Tier 0), and passes through two Tiers (1 and 2). The choice of which Tier is better to use depends on the quality and availability of the required data. In this study it was decided to use Tier 2, which is the more detailed approach for the human health risk assessment and is based on quantitative data. A fundamental step for the work has been the collection of the georeferenced environmental regional data, in a shapefile

format, for the Campania region. On the basis of the available data, the representative parameters of the Source-Pathway-Receptor for the different exposure routes were selected, and are tabulated in Table 2.1. The scores were normalized to 100, even if not all the parameters were available for a certain Source-Pathway-Receptor Indicator.

Table 2.1*: Parameters chosen from the PRA.MS methodology for the human health risk assessment.*

Groundwater (GW)	Surface water (SW)	Air (AIR)	Direct contact (DC)	
Potential hazard map	Potential hazard map	Potential hazard map	Potential hazard map	Source
Lithology of unsaturated zone	Slope	Particulate mobility		Pathway
Infiltration	Flooding risk			
	Surface water flow rate			
Distance of site to drinking water supply	Surface water use	Land use at site	Land use at site	Receptor
	Minimum distance from surface body	Distance to the nearest residential area	Distance to the nearest residential area	

2.2.2. The sources

2.2.2.1. The Hazard map

The first measure that is required in the Tier 2 of the PRA.MS methodology for featuring the Source is the chemical characterization of the soil contamination: first are recognized the chemical elements at each site, then their chemical toxicity and scores are evaluated. The PRA.MS model is not implemented for cases where more than one contaminant is present at the same site. Hence, in the PRA.MS methodology, only the most toxic contaminant, for each exposure route is taken into account.

In the case of a regional risk assessment, the risk at single industrial or mining contaminated sites is not evaluated, but the assessment is extended to cover a wider territory. Using the GIS tool, is it possible to treat each pixel belonging to the regional territory as a potential source. Starting from the chemical characterization of the topsoils samples, covering the entire Campania region (Buccianti et al., 2015), described above, the Hazard map was plotted, with a pixel dimension of 20 m, which contains all the information about the presence, the amount and the toxicity of multiple contaminants.

The determination of the concentration of 53 elements for each sample was useful to elaborate a detailed statistical and cartographical analysis of the Campania region (Buccianti et al., 2015, De Vivo et al., 2016), and is a reference guide for all further elaborations. For the purpose of this study, only the 15 potentially toxic elements (Sb, As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Sn, Tl, V, Zn) for which the Italian legislation (D.Lgs. 152/06) established trigger and action limits were taken into account, by defining the contamination threshold values (CSC) for the amount of chemical elements in topsoils or water samples. The D.Lgs.

152/06 promotes a requalification of human life by an improvement of the environmental quality. The law assumes that, if a contaminant concentration in a soil exceeds the CSC value, a follow-up risk assessment must be carried out at the site. Once a follow-up risk assessment has been carried out, the remediation can be applied only if the contaminant concentration exceeds the risk threshold values (CSR), valid only in the specific site of interest. Two are the CSC values indicated by the legislation, one regarding the hazard in residential sites, and one with a higher value for industrial and commercial sites. Because the CSC values are established for the human health risk, they can be used directly for the definition of the hazard; in particular, the conservative CSC values for residential sites are considered.

The interpolated grids of the spatial distribution of these elements, obtained by multifractal IDW method using the dedicated GIS GeoDAS^{TM} geochemistry software (Cheng, 2003), were the basis for plotting the Hazard map. To each pixel of the interpolated maps, a value of 1 was assigned if the element concentration was above the CSC, and 0 if the element concentration was below the CSC. The produced *Boolean* surfaces clearly show, based on the current legislation, if contamination is present, and consequently a potential hazard for the population. The soil threshold values for the toxic elements, established by the Italian legislation, are for the potential human health risk that may be caused by contamination, and does not take into account the natural geochemical background values related to the different lithologies. In the ArcGIS environment, by means of the Spatial Analysis module, the Boolean surfaces were summed up to obtain a composite additive map of the Hazard (Fig. 2.2a). On the map, the higher values correspond to the areas where there is a contemporary presence of a higher number of potential toxic elements that exceed the threshold values, representing a more intense soil degradation. The map can be used as a Source Hazard characterization for further analysis. The map has been reclassified assigning four scores between 0 and 100 (Fig. 2.2b, Table 2.2).

Table 2.2*: Assigned scores for the Hazard map, characterizing the Source for all Exposure routes. Out of the 15 potentially hazardous elements, only 8 (Zn, Tl, V, Pb, Cu, Cr, Be, As) occur in the Solofrana area; Be, Cd, As, Co, Sn, V, Tl in the southern Cilento area.*

Number of potentially hazarodus elements	Hazard scores
0	0
1 - 2	25
2 - 4	50
4 - 6	75
6 - 8	100

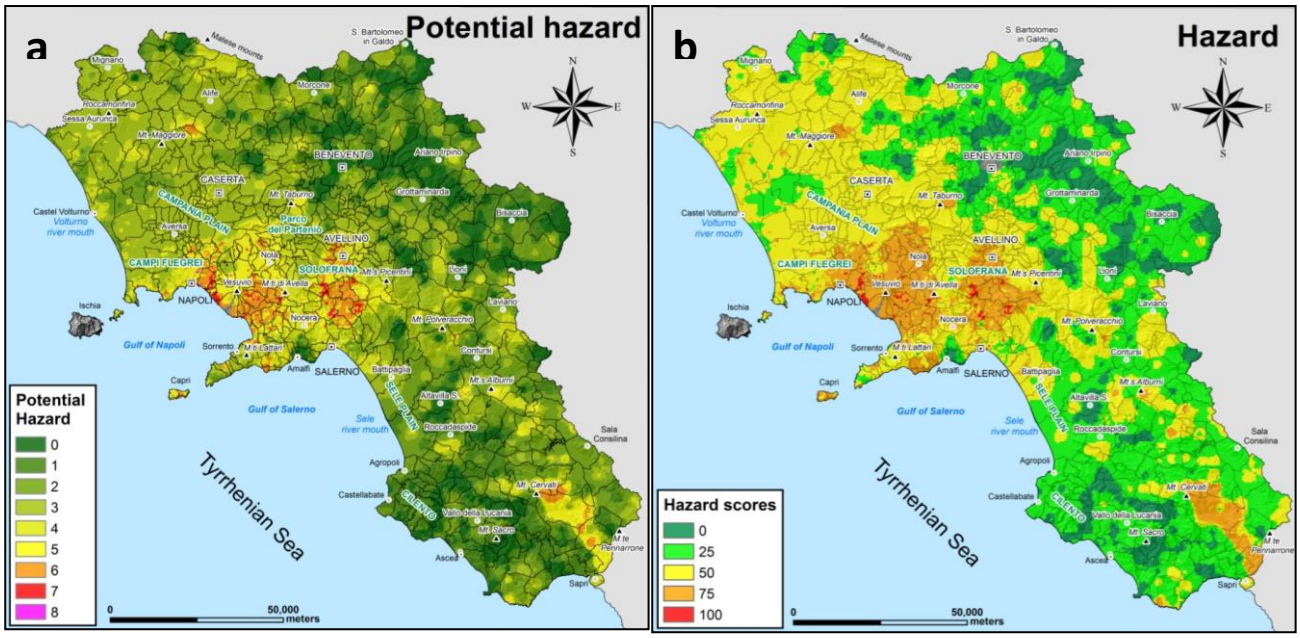


Fig.2.2*: a) Cumulative map of the Hazard due to the presence of potentially toxic elements (Sb, As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Sn, Tl, V, Zn) in the topsoils of Campania region; b) Reclassification of the Hazard map of Campania region according to the scores explained in Tab.2.2.*

2.2.3. Exposure routes

2.2.3.1. Groundwater (GW) map

The GW exposure route map (Fig.2.5) is obtained by means of spatial analysis in ArcGIS software, using the following expression:

$$GW_{er} = (S_{gw} * P_{gw} * R_{gw}) \div 10^4$$

Where:
S_{gw} is the groundwater hazard map
P_{gw} is the GW Pathway Indicator
R_{gw} is the GW Receptor Indicator

The classification of the four exposure route maps is computed with the standard Natural Breaks in the ArcGIS software, assigning four intervals.

The GW Pathway Indicator is represented by the sum of two factors: (a) the lithology of the unsaturated zone and (b) the infiltration rate. The main factor that contributes to the transport of contaminants to the aquifer is the properties of the unsaturated zone that contaminants have to pass through before they reach the aquifer. The weight of this factor, which has the capacity to attenuate the dispersion of contaminants in the groundwater, is 78, while the infiltration rate has a weight of 22. As already explained, the weight of a factor is given the maximum allowed score of that factor in the PRA.MS methodology, normalized to 100. In the PRA.MS methodology the scores assigned to the factor of lithology of the

unsaturated zone are grouped into 4 classes, taking into account the top layer geology, structural and hydraulic properties. In particular it evaluates the vertical hydraulic conductivity. Then other factors are evaluated in order to estimate potential release to groundwater, such as the presence and thickness of any impermeable layer, the aquifer depth from ground surface and the contaminant mobility. All these parameters cannot be evaluated at regional level, due to their variability. Moreover the vertical hydraulic conductivity is not related to the unsaturated zone, because it is usually measured under saturated flow conditions, so it should not be used in connection with a classification relating to vertical flow rates through the unsaturated zone (Lewis et al., 2006).

For scoring the lithology of the unsaturated zone (Fig. 2.3) the hydrogeological map of Campania Region (ISPRA-MAIS) was used. Before applying permeability values to the unsaturated zone (Lewis et al., 2006), this map was reclassified into four classes of scores (Table 2.3a), using the type of hydrogeological complexes of Campania Region and their permeability. The definition of hydrogeological complex is based on the relative permeability, including similar lithologies, with similar type of permeability and with a restricted range of relative permeability. Hence, using the hydrogeological complexes, parameters such as granulometry, fracturing, karstification and the mean annual groundwater discharge are already taken into account. An additional layer that could be evaluated is the permeability of soil (Lewis et al., 2006), especially in the cases where the soil is different from the parent material (e.g. the pyroclastic deposits on carbonate rocks in Campania region), but the intention is to modify as least the original methodology. The permeability of the lithologies of Campania region varies from: medium-high for porosity in the coastal Campanian and Sele plains; very high for the carbonates that form the Apenninic belts, with high effective infiltration due to fractures and karst; low and very low in the north-eastern part of the region, caused by the presence of silt and clay deposits.

Table 2.3: *a) Scoring model for the Groundwater Pathway Indicator; lithology factor scores evaluated through the permeability of the hydrogeological complexe; b) Scoring model for the Groundwater Pathway Indicator; Infiltration factor scores evaluated through the mean annual precipitation values (mm/yr).*

a)

Permeability of hydrogeological complexes	Lithology factor scores
High permeability – fractured igneous rocks and karst limestone	78
Moderate permeability – moderately permeable dolomite, cemented sandstone, molasse, pyroclastic fall deposits	56
Low permeability – clayey silt, less permeable limestone, turbidite	33
Very low permeability – clayey limestone, prevalentely clay	11

b)

Mean annual precipitation (mm/yr)	Infiltration factor scores
< 1100	22
900 – 1100	18
700 – 900	13
500 – 700	9
300 – 500	4
< 300	0

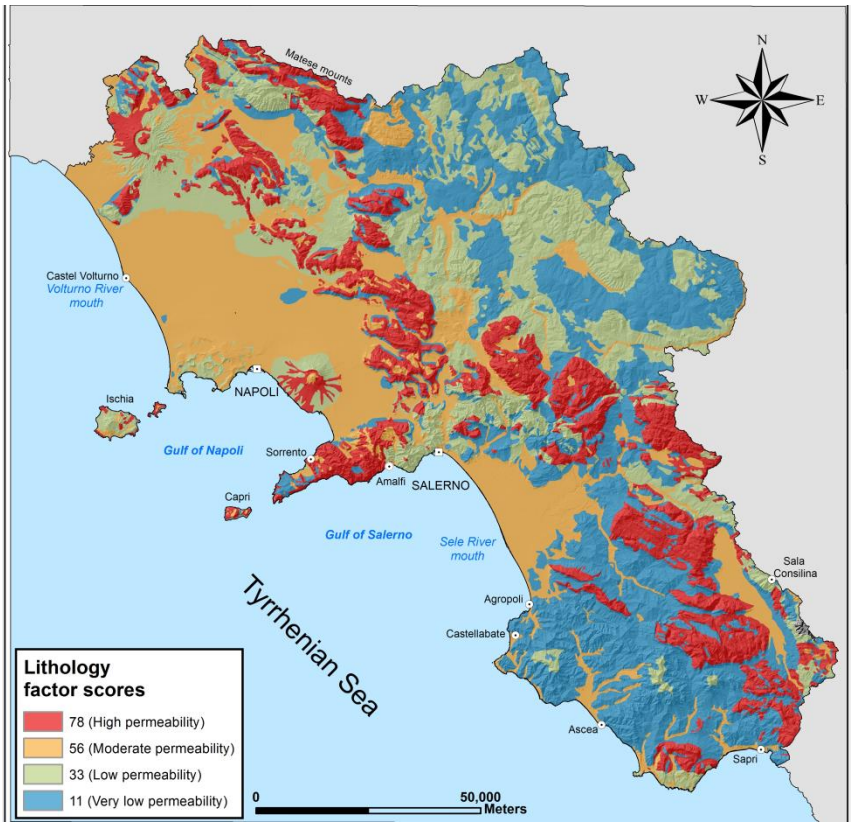


Fig.2.3: *Lithology factor score map*

The infiltration classification and scoring in the PRA.MS methodology are based on mean annual precipitation data. The 28 meteorological stations of the Regional Agrometeorological Network (C.A.R, 2012), covering the whole regional territory, were used (i.e. measurements of precipitation, temperature, humidity, wind velocity and surface soil humidity). In a first attempt, only the precipitation data of the last measured year (considering the total mm of rainfall during 2012 in the different stations) were used. After

that, the mean annual value of the precipitation between 1999 and 2012 was calculated. For the compilation, the data relative to annual precipitation, where one or more months were missing, the data were deleted. Only the stations with more than 50% of the data were considered (i.e. more or equal to 7 years of measurements). Afterwards both the mean and the median values of the data were calculated, and it was found that the mean percentage difference between the mean and the median is about 5%, and only in three cases the difference is significant (20%). The interpolated map of these data was plotted using the standard IDW method.

Looking at the interpolated maps of both mean and median, it can be assumed that the mean values are effectively the most relevant to reality. The measured precipitation has an extremely high spatial variability. Hence, it is important that the interpolation does not smooth out the local variability of the data. The interpolated map was reclassified using the scores tabulated in Table 2.3b (Fig. 2.4). The precipitation in the Campania region is not less than 700 mm/yr. No appreciable differences in the resulting maps of groundwater exposure route and overall risk, among the 2012 precipitation data and the mean annual values between 1999-2012, were observed.

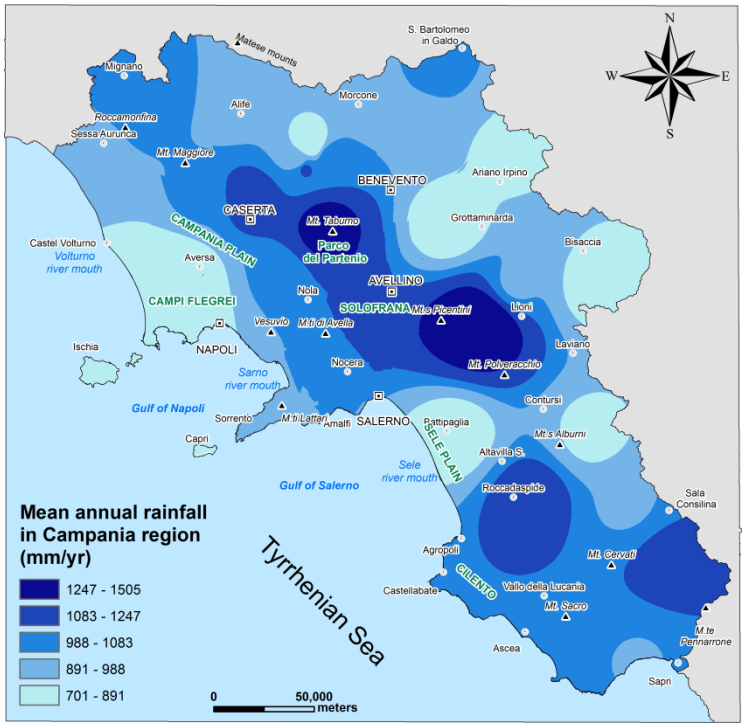


Fig.2.4: *Mean annual precipitation map of Campania region(C.A.R., 2012)*

The GW Receptor Indicator is represented by the distance of the nearest drinking water supply from the source. The available data about the drinking water supply in Campania come from the ISPRA-MAIS database. The map of the distance is computed by means of the Euclidean Distance tool in ArcGIS software and is reclassified according to the scores of Table 2.4.

Table 2.4*: Scoring model for the Groundwater Receptor Indicator, by means of the distance of the Source from the nearest drinking water supply.*

Distance from the drinking water supply (m)	Distance factor scores
0 – 150	100
150 – 400	86
400 – 900	71
900 – 1500	57
1500 – 3000	43
> 3000	29

The maximum scores for the GW pathway Indicator (80 – 100) are located along the Apennine belt, which correspond to the zone with the highest permeability of the unsaturated zone and with the highest mean annual precipitation. Between 60 and 80 are the scores in the Campanian plain along the coast, where the precipitation is lower, but the permeability of the unsaturated zone is still quite high, with a score of 56.

The final GW exposure route map (Fig. 2.5) is affected by the location of the drinking water supplies on the carbonate rocks, so that the maximum scores for this exposure route are located nearby the drinking water supply wells (between 16 and 75). Scores between 7 and 16 are found on the remaining Apennine belt and on the Campanian plain, while the remaining territory, with low permeability, low precipitation and no drinking water supply, have scores between 1 and 7.

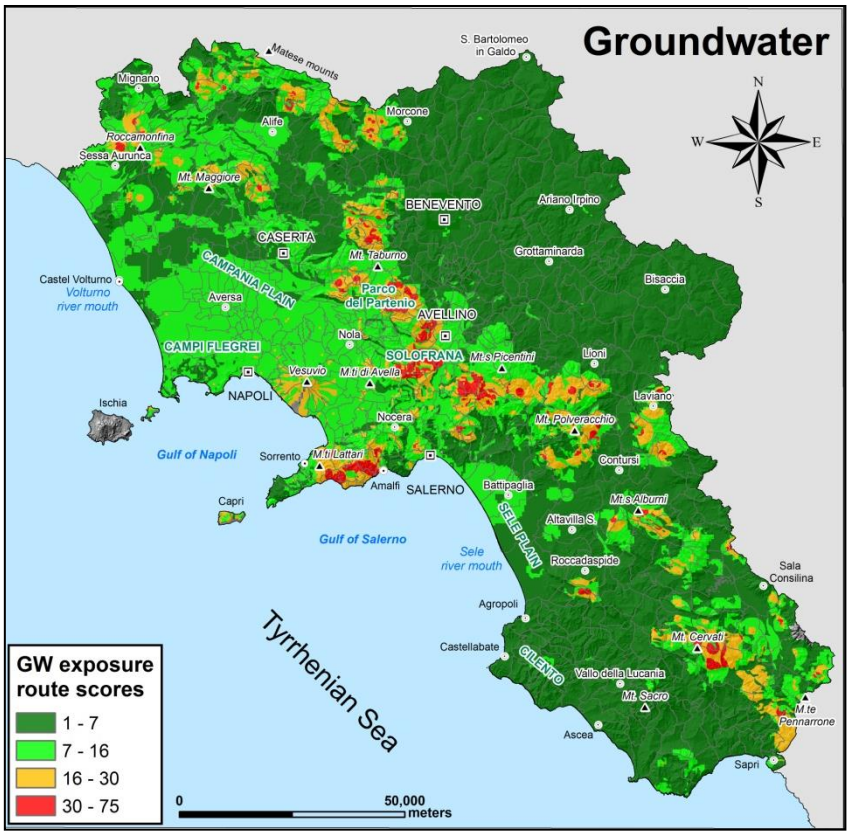


Fig.2.5: *Groundwater (GW) Exposure Route map for Campania region.*

2.2.3.2. Surface water (SW) map

The SW exposure route map (Fig. 2.7) is obtained by means of spatial analysis in ArcGIS software, through the following expression:

$$SW_{er} = (S_{sw} * P_{sw} * R_{sw}) \div 10^4$$

Where:
S_{sw} is the surface water hazard map,
P_{sw} is the SW Pathway Indicator
R_{sw} is the SW Receptor Indicator

The SW Pathway Indicator, explaining the potential of contaminants to be dispersed in the surface water, depends on three factors: the terrain average slope, the flooding risk and the surface water flow rate.

For the average slope map (Fig. 2.6) the Digital Terrain Model 20m for the Campania region was used. The grid was reclassified into four classes of slope (Table 2.5a), with the highest scores corresponding to the highest slopes, which have a large amount of run-off that contribute to the migration of contaminants in surface water. The floodplain map of the Campania Region, available from the SIT database (Geographic Information System, 2008),

did not contain the information about the flooding return periods, and this is due to the extreme heterogeneity of the data elaborated from the different Basin Authorities. Hence, the reason for only producing a Boolean surface, assigning the maximum allowed score for the flooding risk (31) indiscriminately to all the floodplain areas, and a score of zero for the remaining territory. The surface water flow rate map was obtained from the surface water map of Campania region, available from the project DBPrior10K. The surface water body types were differentiated with respect to stream size and stream order (Table 2.5b). The scores are higher for low stream orders, because there is a general decreasing trend of contaminant concentrations with increasing stream order, explained by a dilution effect (Kang et al., 2008).

Tale .2.5: *a) Scoring model for the Surface Water Pathway Indicator; slope factor score; b) Scoring model for the Surface Water Pathway Indicator; surface water flow rate factor scores by analyzing the stream orders.*

a)

Slope	Slope factor scores
> 8%	44
5% - 8%	26
2 % - 5%	18
< 2%	9

b)

Surface water body type – stream order	Surface water flow rate factor scores
Order 1 – Small to moderate stream	25
Order 2 – Moderate to large stream	20
Order 3 – Large stream to river	15

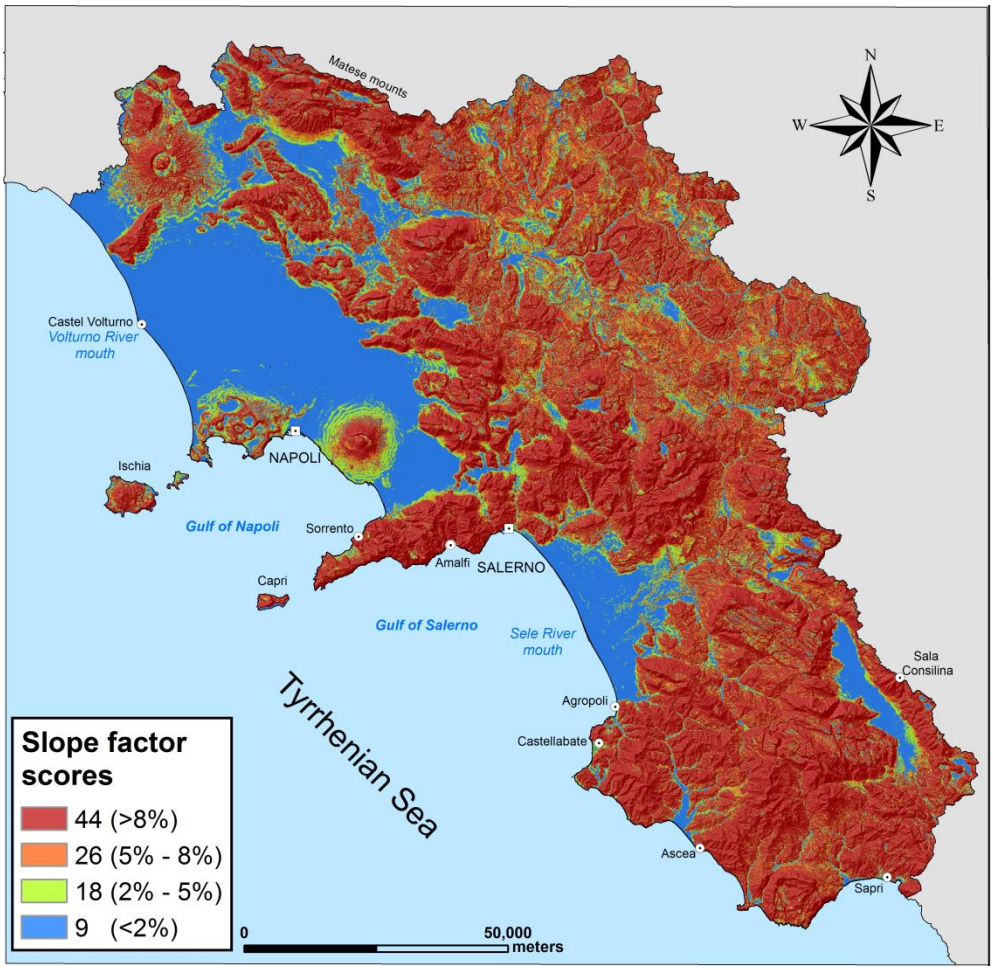


Fig.2.6: *Average slope map, reclassified according Table 2.5a.*

The SW Receptor Indicator is the minimum distance of the surface water body from the source. The Euclidean Distance map was developed from the same surface water map of Campania region used previously, and then reclassified to 6 classes of scores (Table 2.6). To these scores, the value of 46 was added; it is assumed, in fact, that the most common surface water use in Campania region is the irrigation with food crop, having the score of 46 in the PRA.MS methodology.

Table 2.6: *Scoring model for the Surface Water Receptor Indicator, by means of the distance of the Source from the surface water bodies. To these scores a value of 46 was added (see text).*

Distance from the surface water bodies (m)	Distance factor scores
< 200	30
200 – 850	24
850 – 1700	18
1700 – 2600	12
2600 – 3600	6
> 3600	0

The final SW exposure route map (Fig. 2.7) shows the main areas with higher vulnerability of the surface water bodies; the first is between the Avellino and Salerno provinces, and the second is in the south eastern part of the Cilento area.

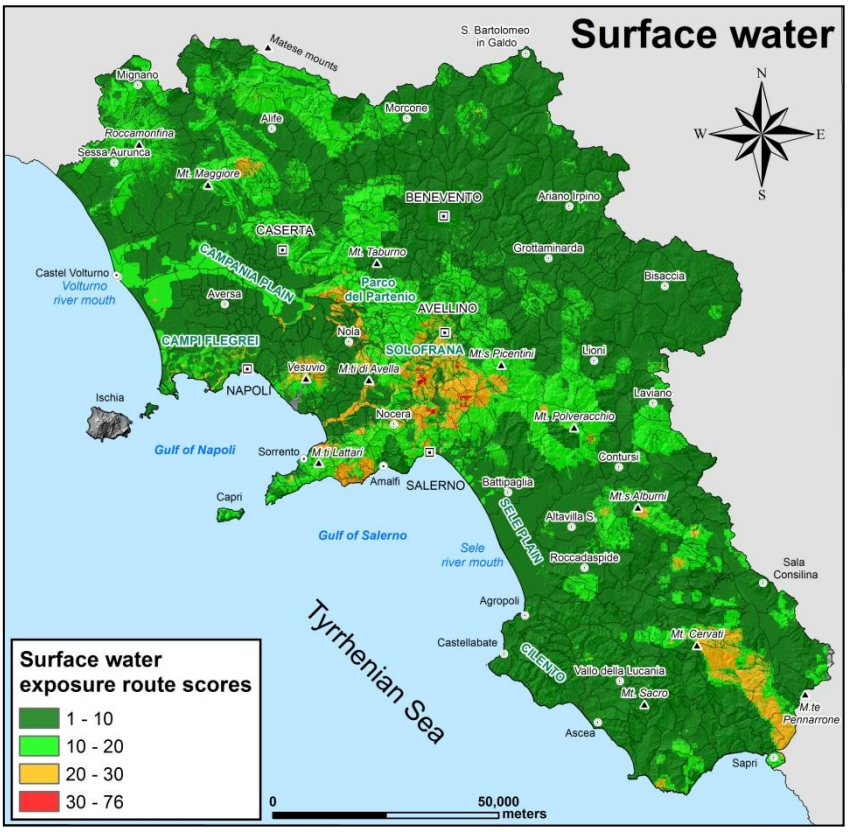


Fig. 2.7: *Surface water (SW) Exposure Route map for Campania region.*

2.2.3.3. Air particulates map

The Air particulates exposure route map (Fig.2.9) is obtained by means of the spatial analysis module in ArcGIS software, through the following expression:

$$Air_{er} = (S_{air} * P_{air} * R_{air}) \div 10^4$$

Where:

S_{air} is the Air particulates hazard map

P_{air} is the Air particulates Pathway Indicator

R_{air} is the Air particulates Receptor Indicator

The only parameter that characterizes the Air particulates Pathway Indicator is the Particulate Mobility, related to the possibility for the soil solid particles to be transported away from the contaminated source. The particulate mobility, through the De Martonne Aridity Index (AI), was evaluated using the same meteorological data described for the GW Pathway Indicator characterization. The AI is estimated by the following formula:

$$AI = P \div (T + 10)$$

Where:

P is the mean annual precipitation (mm/yr)

T is the mean annual temperature (°C)

The assigned scores for the Particulate Mobility factor based on the AI are explained in Table 2.7. The AI in Campania region varies between 26 and 64, so the Air Particulates Pathway Indicator, represented by the Particulate Mobility factor, has only scores of 66 or 33.

Table 2.7: *Scoring model for the Air particulates Pathway Indicator based on the De Martonne Aridity Index values.*

Aridity Index	Particulate mobility factor scores
< 25	100
25 – 42	66
42 - 74	33
> 74	0

The Air particulate Receptor Indicator is evaluated by two factors: land use at site, and distance from the nearest residential area. The Corine Land Cover 2012 map was used for classifying the land use (Fig. 2.8). From the same map the urban areas were extrapolated, and produced the Euclidean distance map through the ArcGIS spatial analysis module, which calculates the distance of each point (Source) from the residential areas. The scores for both factors are indicated in Table 2.8a and b.

Table 2.8*: a) Scoring model for the Air particulates Receptor Indicator; land use as site factor; b) Scoring model for the Air particulates Receptor Indicator; dstance of the Source from the nearest residential area.*

a)

Land use at site	Land use factor scores
Residential	60
Park/School/Beaches	51
Agricultural/Livestock	36
Industrial/Commercial	26
Isolated areas	0

b)

Distance from the nearest residential area (m)	Distance factor scores
< 400	40
400 – 1070	27
1070 – 2200	20
2200 – 3350	14
> 3350	7

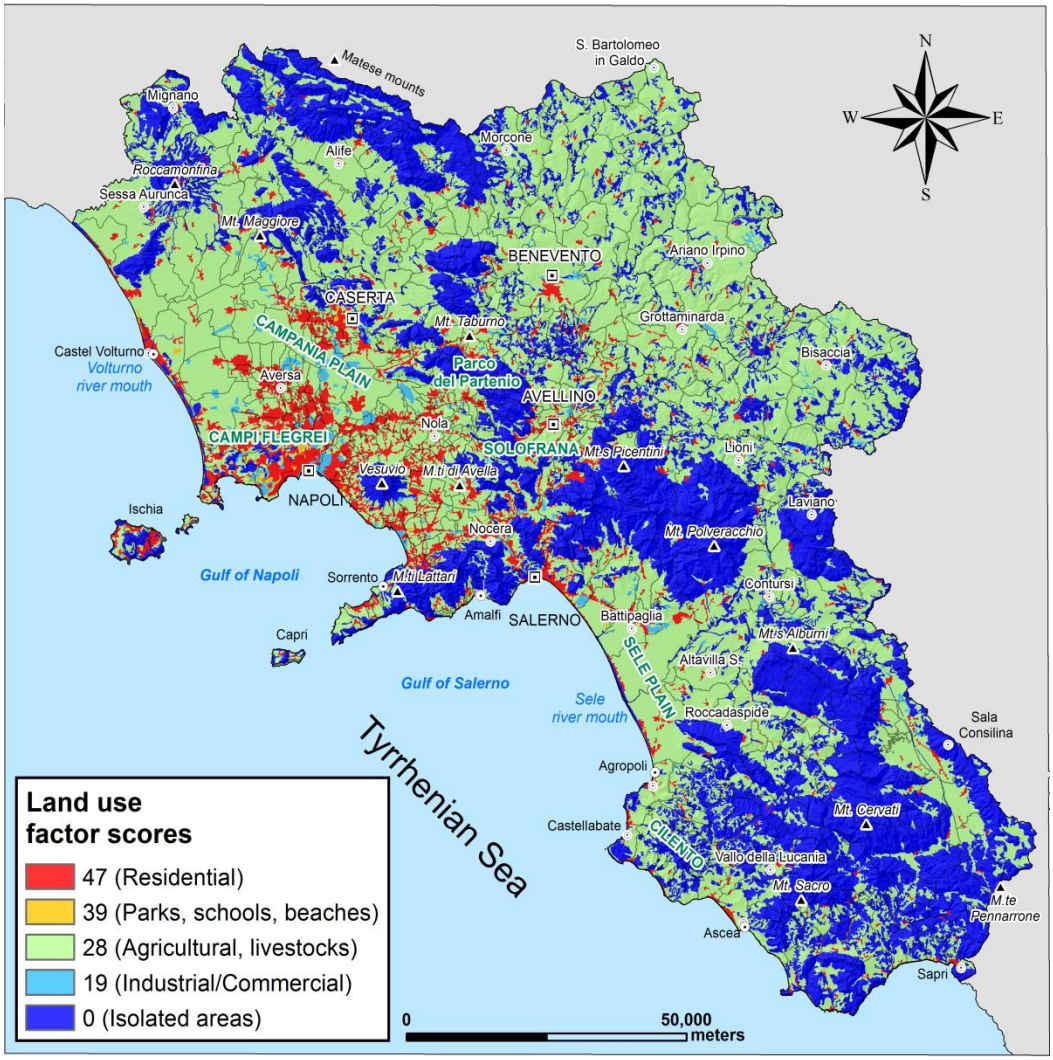


Fig. 2.8: *Corine Land Cover map reclassified according Table 2.8a.*

The factor that mostly affects the Air particulates exposure route map (Fig. 2.9) is the presence of residential areas. The highest scores (between 33 and 66) were found mainly in the Neapolitan province and on the Sarno River plain, and sparsely on the Lattari Mounts, Salerno urban area, Sele river plain and in south Cilento. Values between 23 and 33 were found in the same urban areas, in particular in the Campi Flegrei area and in the Campania plain. Some sparse value between 23 and 33 can be also found in the Avellino province, in Caserta province , from Alife to Trebulani Mounts (Mt. Maggiore) to Roccamonfina volcano (Sessa Aurunca), on the Volturno and Sele river plains and in south Cilento area. Scores between 13 and 23 are still in the main urbanized areas, from the Neapolitan province to Caserta, Avellino and Salerno. The remaining inland territory, comprising mostly agricultural and isolated areas, has the lowest scores (0-13).

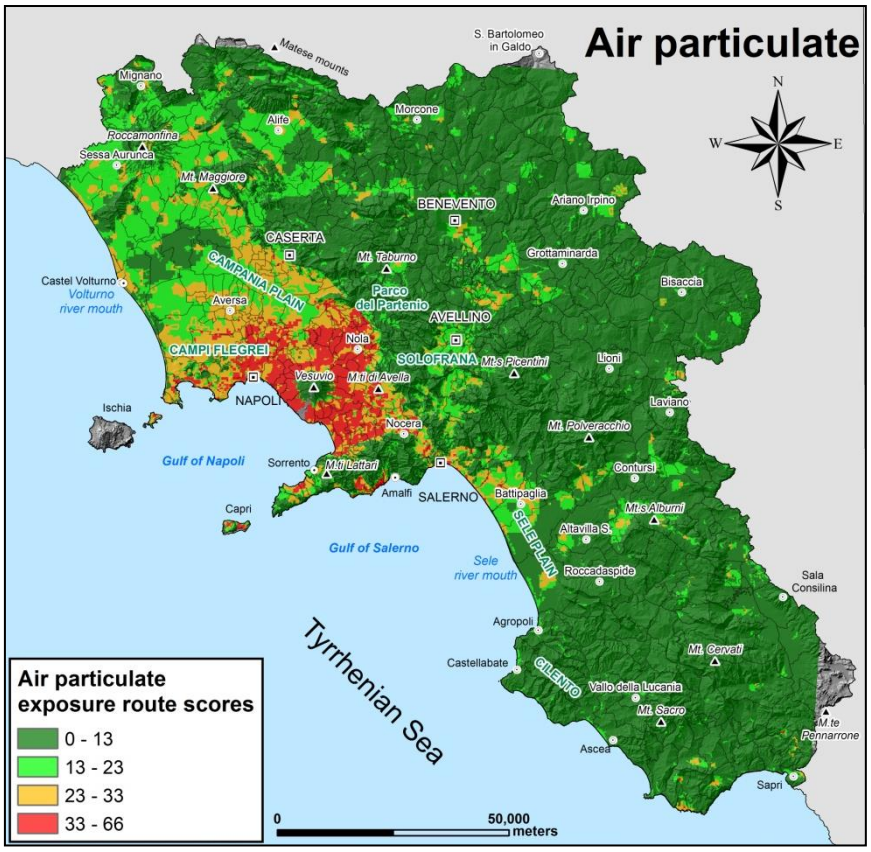


Fig. 2.9: *Air particulate Exposure Route map for Campania region.*

2.2.3.4. Direct contact (DC) map

The DC exposure route map (Fig.2.11) is obtained by means of the spatial analysis module in ArcGIS software, through the following expression:

$$DC_{er} = (S_{dc} * R_{dc}) \div 10^2$$

Where:
S_{dc} is the direct contact hazard map
R_{dc} is the DC Receptor Indicator.

For the DC exposure route the Pathway is not relevant, because it is assumed that the Source is coincident with the Receptor. What determines the vulnerability for the Receptor in this case is the type of land use and the distance from the Source. The Corine Land Cover map and the Euclidean distance map for the urban areas (Fig. 2.10) were used, and both reclassified according to the scores in Tables 2.9a and b.

Table 2.9: *a) Scoring model for the DC Receptor Indicator; land use at site factor; b) Scoring model for the DC Receptor Indicator; distance of the Source from the nearest residential area.*

a)

Land use at site	Land use factor scores
Residential	47
Park/School/Beaches	39
Agricultural/Livestock	28
Industrial/Commercial	19
Isolated areas	0

b)

Distance from the nearest residential area (m)	Distance factor scores
< 400	53
400 – 1070	38
1070 – 2200	29
2200 – 3350	19
> 3350	8

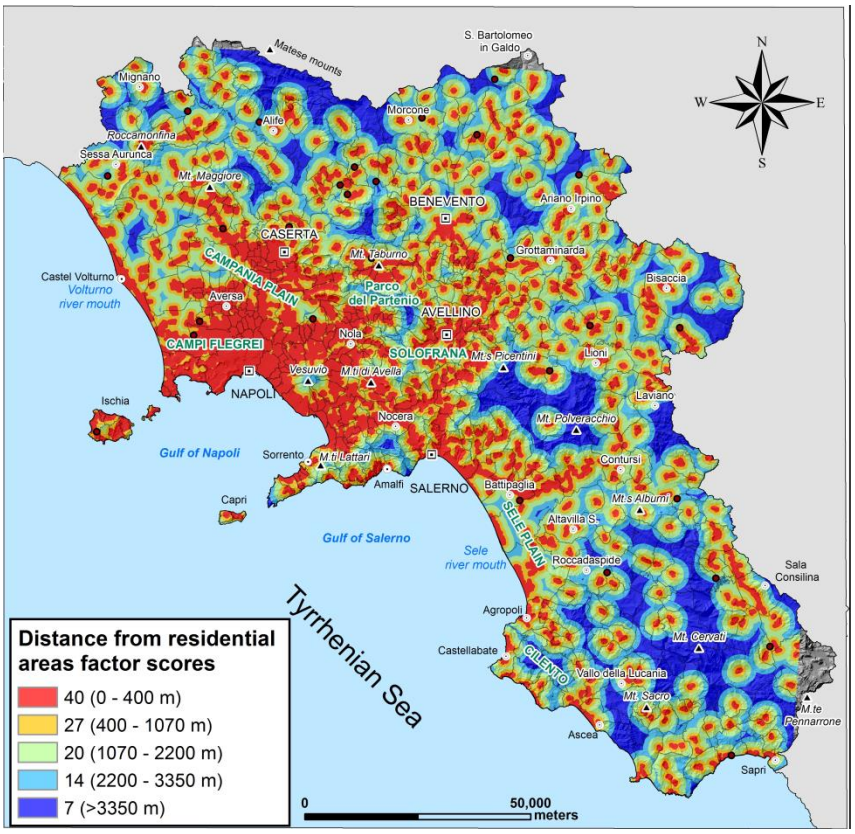


Fig. 2.10*: Euclidean distance map from the nearest residential area, reclassified according Table 2.9b*.

In this case, the main factor conditioning the vulnerability of human health is the presence of residential areas near a potential contaminated site. Combining the highest scores of the hazard map and the DC factors, the DC exposure route with the main impact (having scores between 34 and 100) was obtained in the metropolitan area of Naples, and in the area between Avellino and Salerno provinces (Fig. 2.11).

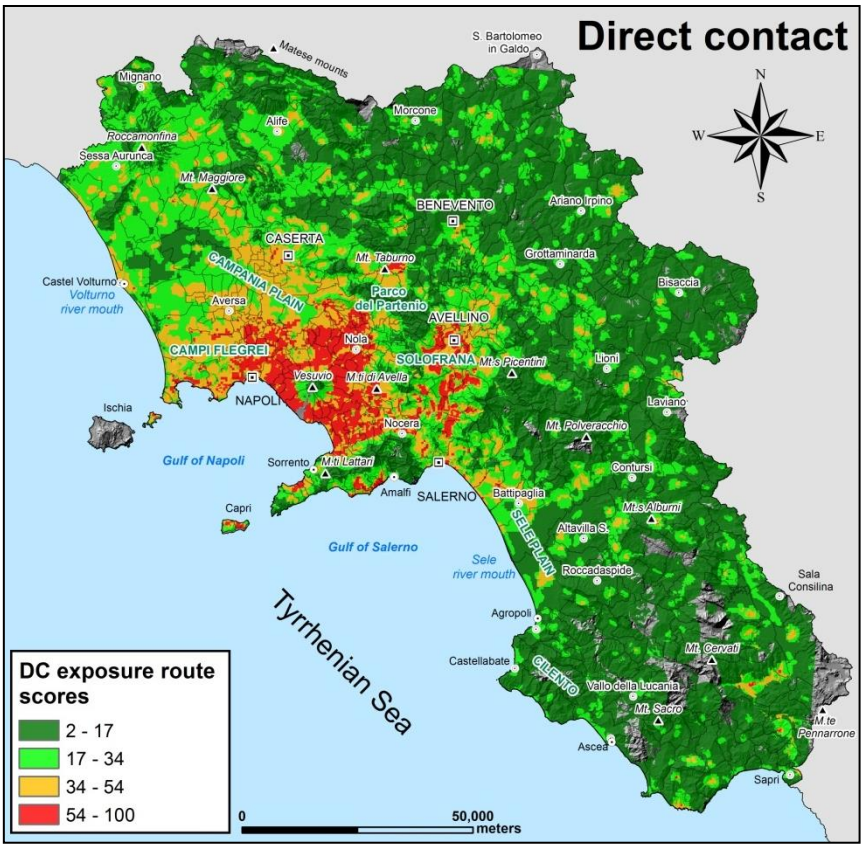


Fig. 2.11: *Direct contact (DC) Exposure Route map for Campania region.*

2.2.4. Human health risk map

The overall human health risk map (Fig. 2.12) is computed by the root mean square of the four exposure routes, using the following algorithm (EEA, 2006):

$$R = \sqrt{(GW_{er}^2 + SW_{er}^2 + Air_{er}^2 + DC_{er}^2) \div 4}$$

Where:
GW_{er} is the Groundwater map.
SW_{er} is the Surface water map
Air_{er} is the Air particulates map
DC_{er} is the Direct contact map

The map of the human health risk has been classified according to four classes of risk: very low, low, medium and high risk.

The PRA.MS methodology provides also an uncertainty analysis on the overall human health risk score, that reflects the quality of the data. The uncertainty analysis takes into account the influence in final site score of not available and not accurate input data, such as the use of geo-referenced data of low resolution. Assessments carried out with generic and low accuracy data may result in very high, and sometimes unacceptable, uncertainties (EEA, 2005b). The original calculations exposed in the PRA.MS for the uncertainty cannot

be applied in this case, because geo-referenced data are considered. At a single industrial site it was possible to collect specific information for characterizing the parameters in a restricted area. In this case each pixel is considered to be a possible source. The uncertainty in such a case is not related to missing data, but is dependent only on the resolution of the geo-referenced data. In the Campania region risk assessment, the pixel resolution for all plotted maps is 20 m. The main uncertainties are related to: (a) the Boolean surfaces produced for the SW Pathway Indicator, due to the absence of flooding return periods information in the floodplains; (b) the assumption for the SW Receptor Indicator that the most common surface water use in all Campania region is the irrigation with food crops; (c) the use of the low-density meteorological information of the Regional Agrometeorological Network for the elaboration of the Air particulates and (d) the GW Pathway Indicators maps. An implementation is required in a follow-up work for quantifying the uncertainties.

Fig. 2.12*: Overall Risk map for human health risk assessment in Campania region.*

2.3 Results and discussion

The dominant exposure route is the Direct Contact, reaching scores up to 100 in the Neapolitan province, and in the area between Avellino and Salerno. This means that the main risk for the population in these areas comes from the direct contact with the soil that potentially contains pollutants. The risk is increased by the fact that the Neapolitan, Salerno

and Avellino provinces have the higher number of residents, between 20,000 and 50,000 (Fig. 2.13). Moreover, intense agricultural and viticulture activities are diffused in the same areas. Secondary exposure routes, with scores reaching 75, are contamination of groundwater, surface water and diffusion in air. The overall risk map shows a similar situation, with the maximum risk, up to 63, restricted to the Neapolitan area, and mainly in the eastern area of the city. Moderate risk, with scores between 40 and 60, can be found in all the metropolitan area of Naples and province, from Campi Flegrei to Aversa, to Sarno river plain, and the area between Avellino and Salerno.

The aim of this work was to identify potential hazardous areas in the Campania region, and to prioritize them in order to use more efficiently the available resources for more detailed studies, and if needed their remediation. Potentially hazardous areas are defined in the PRA.MS as areas where the soil contamination does not affect only the local environment, but poses significant risks to human health and/or ecosystems (Quercia et al., 2006). Here there are conditions that allow the contamination to spread into the environment, and reach the population in different forms, such as inhaled dust or through the food chain. While the starting point of the PRA.MS is a preliminary identification of potentially hazardous areas, and the aim is their scoring, the starting point should be the chemical characterization of the regional territory in order to locate precisely the potentially hazardous areas. For these areas, there is the necessity to obtain more detailed data and information. Hence, the next step is high-density sampling and a follow-up risk assessment of selected areas.

The previous regional methodologies were based on selected industrial and mining sites (EEA, 2005b, Pizzol et al., 2011), resulting in a scoring of those sites, or on the effects of a single contaminant (Tristán et al., 2000). The new approach can help to obtain a multielement characterization of a whole regional territory. Each pixel on the maps shows a portion of territory, and, in the final risk map, indicates how much that territory is subjected to contamination. In order to obtain this, all the possible exposure routes have been taken into account. The quality and density of the initial data is fundamental for reaching an assessment as close as possible to reality.

On a wide and industrialized territory, such as the Campania region, is very difficult to understand where to install monitoring systems. Some areas with a score of 75 on the hazard map become, in the final risk map, areas with low risk. This means that the application of the methodology and the elaboration of the overall risk map do not change the general distribution of the hazard, but narrow the limit of the areas of interest, giving a first contribution for the identification of priority areas.

The risk assessment has identified two areas that can be characterized as "potentially hazardous". The first one is the Neapolitan area, which has been the subject of many

previous published works, with detailed sampling and characterizations (De Vivo et al., 2006b; Cicchella, 2000; Cicchella et al., 2003, 2005, 2008d; De Vivo and Lima, 2008). The second is the area between Avellino and Salerno, which is part of the agricultural zone with a low soil sampling density. The high population density, the presence of viticulture activities, with intense use of fertilizers, and the existence of industries (tanneries that are the main cause of one of the most contaminated sites in Italy, the Solofrana and Sarno River), make this area "potentially hazardous", as shown by the results of the regional risk assessment, and the Figure 2.14 (modified from Quercia et al., 2006). Industrial and agricultural wastes can seriously affect the groundwater, especially in an area with a high number of drinking water supply wells; due to the high slopes, the surface water bodies, which flow to one of the most important rivers of the Region (Sarno river), can carry diluted contaminants and, of course, a high number of residential population is clearly exposed to the contaminated media.

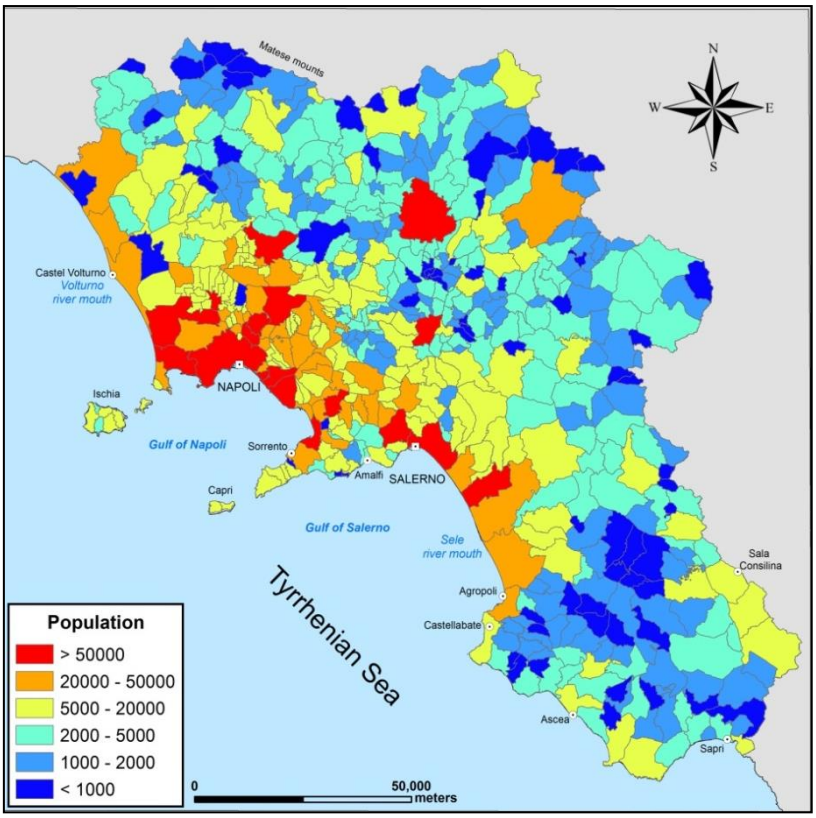


Fig. 2.13*: Municipality based distribution of population in Campania region.*

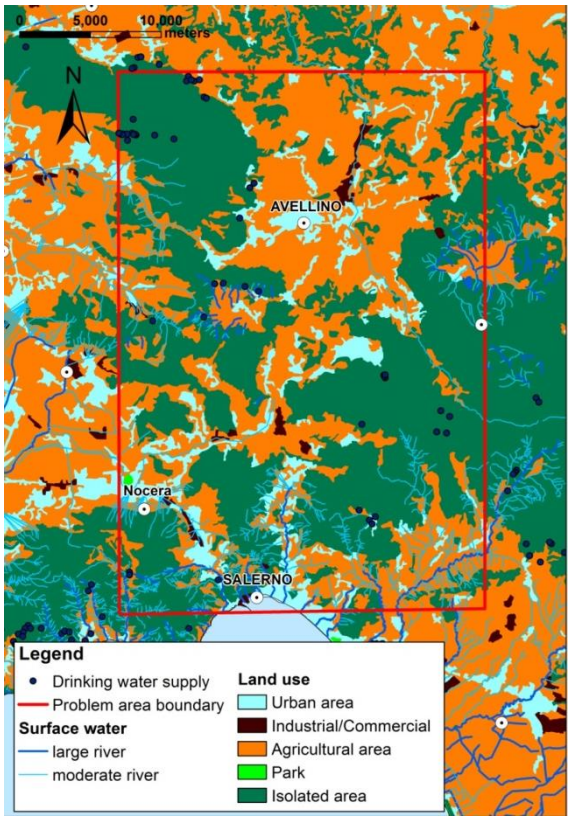


Fig. 2.14: *Individuated potentially hazardous area, located between Avellino and Salerno provinces.*

The identified potentially contaminated area from this regional risk assessment is still too wide to be directly used by the administrations for planning any environmental reclamation and rehabilitation. However, the methodology is useful to identify well-suited areas for a follow-up surveys by increasing the sampling density. Then the same risk assessment methodology described here, can be applied in each area. The denser sampling in the smaller area will provide more precise information about the human health risk, and can be helpful in the planning of follow-up steps. The developed risk assessment methodology should be applied in each area, as the objective is to give to the administrations a valid tool in the decision-making process with respect to land use. The risk map showing the distribution of potentially hazardous areas, should simplify the decision process about the end land use of each area. Another possible advantage of having a regional mapping of environmental risk is the application in epidemiological studies, already carried out by Albanese et al. (2013). They found that there is a good spatial correlation between the incidence of some cancer types and the distribution patterns of contaminants in stream sediment. The use of the regional risk map would be more appropriate than the single element distribution maps, as it provides a more complete views of the environmental and sanitary risk.

Chapter 3 – Follow-up geochemical survey on selected area (Avellino-Salerno-Sarno river basin-Picentini Mts.)

Minolfi et al., *Geochemical follow-up survey in Avellino-Salerno-Sarno river basin-Picentini Mts. area*. In progress

3.1 Introduction

In this chapter, I discuss the geochemical analysis made on the follow-up potentially hazardous area selected by the regional risk assessment. It includes the sampling activity, the sample preparation, the organization of the database, the statistic and cartographic elaboration. Finally, the new GIS based risk assessment methodology has been applied. Although more detailed data for the parameters were not available, the higher resolution lead to identify the areas where follow up risk assessment should be carried out, in order to permit the administrations to guaranteeing the safety of the population.

3.2 Study area

The selected potentially area is 220 km^2 wide. It is located in the central part of Campania region, including the coastline of Salerno and Avellino city, confining with the Lattari Mts. (to the SW), Sarno river basin (on the W), Partenio regional park (on the NW), Benevento (to the N), Picentini Mts. (to the E), and Tyrrhenian sea (to the S).

3.2.1. Geology and geomorphology

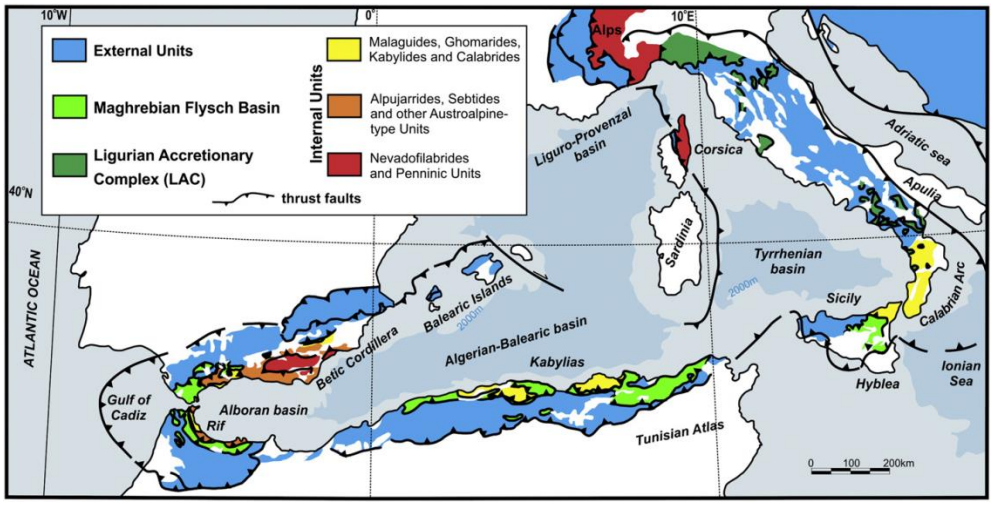


Fig. 3.1: *Tectonic sketch of western-central Mediterranean orogenic belts (from Vitale and Ciarca, 2013, modified from Mazzoli and Martin-Algarra, 2011).*

The southern Appennines are a fold-and-thrust belt characterized by a dominant E/NE tectonic vergence (Vitale et al., 2017 and references therein), part of a wide Alpine orogenic

belt (Vitale & Ciarcia, 2013, Fig. 3.1). The region can be distinguished in (Patacca and Scandone, 2007 and references therein):

- The Tyrrhenian area, characterized by oceanic crust and thinned continental crust, representing a backarc extensional feature developed at the rear of the Apennine system in late- and post-Tortonian times;
- The "real" mountain chain, formed by a deep-seated carbonate duplex system, composed of shallow water and subordinate deeper-water Mesozoic-Tertiary carbonates, stratigraphically covered by Pliocene terrigenous deposits;
- The Southern Apennine foredeep basin, corresponding to the youngest flexural depression developed at the front of the thrust belt, filled by Plio-Pleistocene deposits;
- The Adriatic-Apulia foreland, constituted of Mesozoic-Tertiary carbonates and Triassic evaporites, overlying a thick pile of mixed carbonate-siliciclastic Paleozoic deposits, and a Precambrian crystalline basement.

The selected area is in the northern part of the southern Apennine arc. Four main tectonic complexes can be distinguished (Vitale et al., 2016, Vitale & Ciarcia, 2013 and references therein, Fig. 3.2): (i) the Ligurian Accretionary Complex, part of the inner domain, and formed by Nord-Calabrese, Parasicilide and Sicilide Units; (ii) the Apennine Platform Units and (iii) the Lagonegro-Molise basin Units, both part of the external domain; (iv) the Apulian platform Units, with the exposed Apulian carbonates representing the foreland of the Apennine chain.

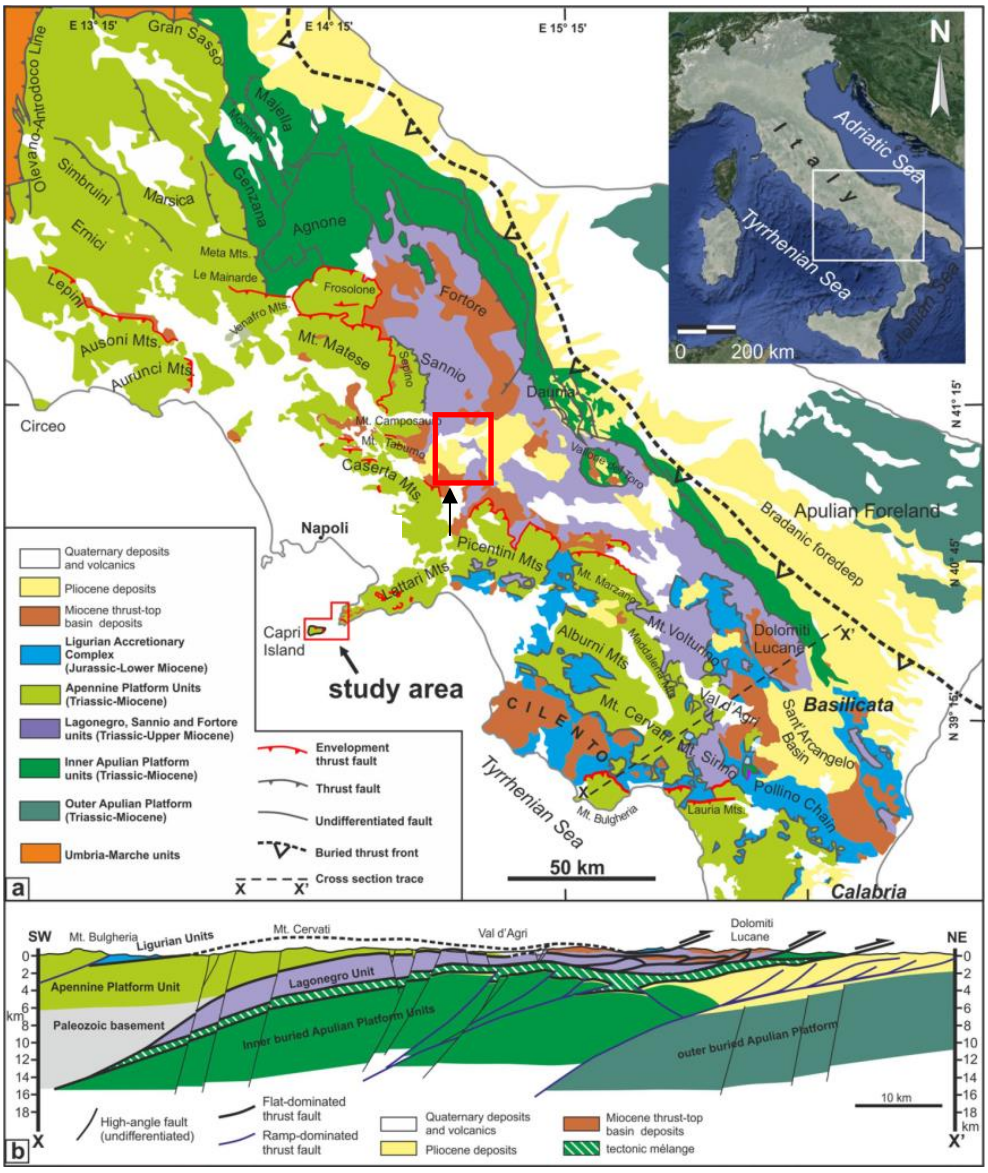


Fig. 3.2: *a) Geological map of the southern Apennines; b) cross section (from Vitale et al., 2016).*

In the study area, only the Apennine Platform Units (Picentini Mounts – Taburno Unit), and a small section of the Sicilide Unit outcrop, together with Miocene (Altavilla Unit in the south and Internal Irpine Unit in the north) and Quaternary (alluvial and pyroclastic) deposits (geological map of Campania region, Bonardi et al., 1988).

From the geological (Fig. 3.3) and land system (Fig. 3.4) maps (SIT GEOPortale, 2008), it is possible to generally distinguish the following deposits:

- Limestone and dolomite with pyroclastic overlay on the high mountainous areas limestone and dolomite; limestone and dolomite with bauxite; limestone and dolomite with marly levels or with flint;
- Conglomerate, sandstone, torbidites, and mudstones on the northern hills and on the E of Salerno city (these areas are probably protected from the pyroclastic fallout by the presence of high mountains);

- Marl, pelite, argillite, generally clayey hills with pyroclastic overlay on the depression of Avellino city;
- Clay deposits without pyroclastic overlay occur on the eastern side of Salerno city, and in a central area around Avellino city;
- Pyroclastic deposits from Somma-Vesuvio (trachite, latite, phonolite and basalt) occur on the western side of the study area, along the Sele plain;
- Quaternary alluvial deposits (occur along the main urban areas).

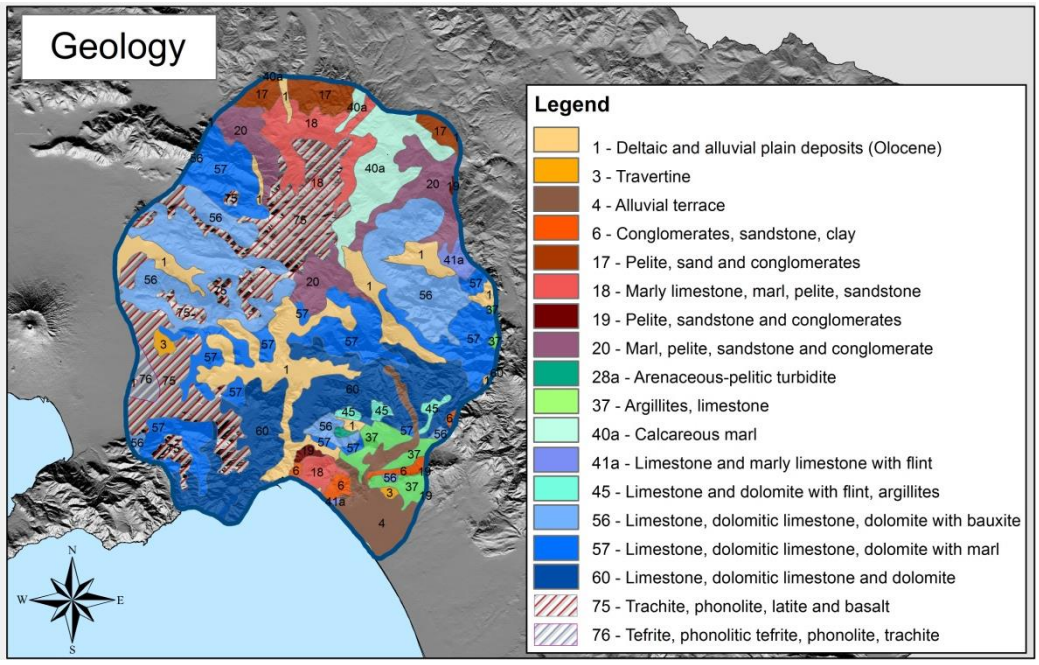


Fig. 3.3: *Geological map of the selected area (from SITGeoportale, 2008).*

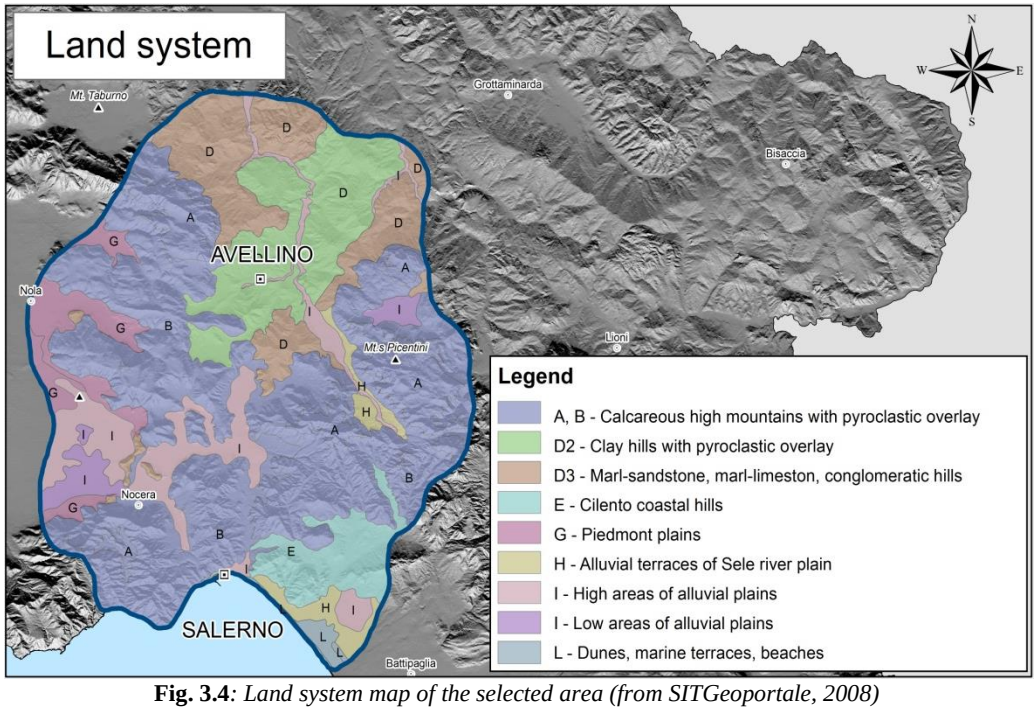


Fig. 3.4: *Land system map of the selected area (from SITGeoportale, 2008)*

The Tyrrhenian sector of the Apennines arc shows a lot of *graben* structures as result of the extensional forces linked to the rifting of the Tyrrhenian Sea associated to the west subduction of the African Plate under the European plate (Buccheri et al., 2002 and references therein). Examples of those structural depressions (perityrrhenian basins) are the Campania plain, the Gulfs of Napoli and Gaeta, and the areas of interest, the Gulf of Salerno and the Sele River Plain on land.

The Gulf of Salerno - Sele River Plain *graben*, trending WSW-ENE, is bounded by NW-SE normal faults with an offset of about 3000 m (Brancaccio et al., 1986; Russo, 1990) of the Mesozoic and Caenozoic Apenninic Units. The formation of the Gulf of Salerno-Sele Plain began in the Tortonian, as testified by Tortonian-Messinian marine sediment distribution (Buccheri et al., 2002). After that, tectonic movements lead to an alternation of erosional and depositional phases, while the subsiding external areas were episodically interested by marine transgression (Fedele et al., 2008). The Plio-Quaternary sediments filling the plain are 1000 m thick (Ippolito et al., 1975; AGIP, 1977; Bartole et al., 1984). The Gulf of Salerno is bordered on the N by a listric fault, which caused subsidence in the sea (Gulf of Salerno) and uplift on land (Sele Plain) (Budillon et al., 1994).

The tectonic movement during Plio-Pleistocene, lead to the formation of Campania *graben* as well, of which the Sarno river plain represents the southern edge. The gradual lowering of the Campania Plain is contemporary, with the filling-in of thick successions of continental, marine and transitional deposits, as well as volcanoclastic materials with different petrographic compositions (De Pippo et al., 2006), from Somma-Vesuvio volcano and Phlegraean volcanic fields, both related to the extensional phases. In the study area, we find the Solofrana River valley that constitutes the inland portion of the Sarno plain, together with the torrent Cavaiola, both connected to the Sarno plain between the San Mauro and Albino Mounts (Fig. 3.5) (Zampella, 2005). Solofrana River valley is surrounded by the Lattari Mountains (S), the Sarno Mountains (N), and the Picentini Mountains (E), covering an area of approximately 3000 ha of cultivated soils. The Meso-Cenozoic calcareous rocks are found at a depth of 2000 m in the Sarno river basin, as basement for the Quaternary deposits of Campania plain. In the Solofra basin the depth reduces to 200-380 m, for an uplift of calcareous rocks that verified during Plio-Pleistocene (Zampella, 2005).

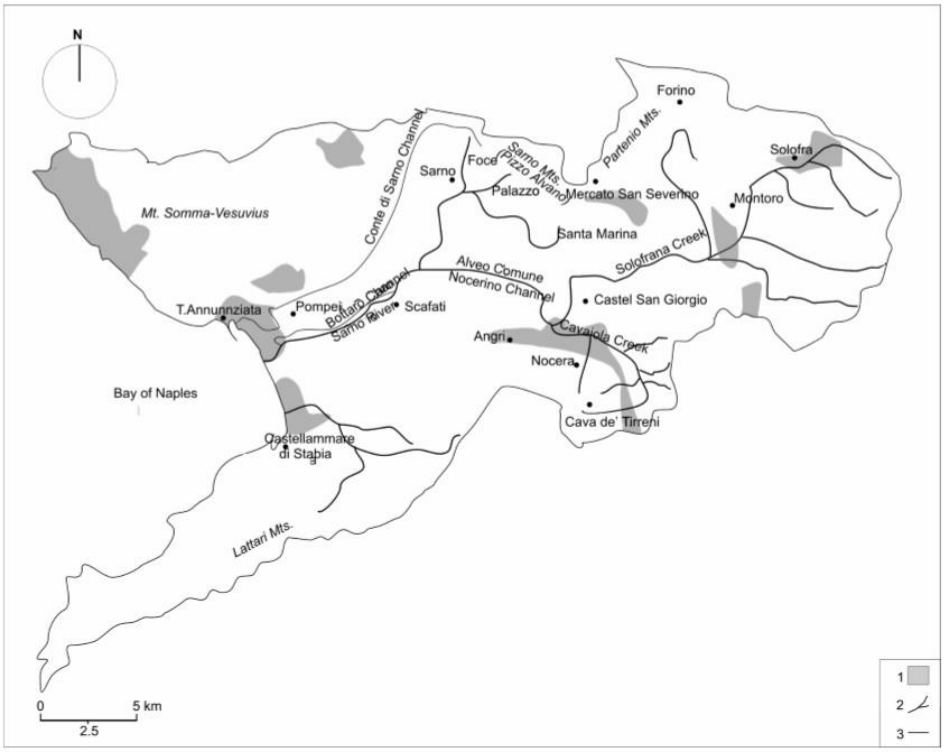


Fig. 3.5: *Water basin of Sarno River and location of the main urbanized and industrial areas: 1) urban and industrial zone; 2) hydrographical network; 3) basin watershed (from De Pippo et al., 2006).*

The slopes of the Solofrana River Valley are between 1 and 5% and the elevation ranges from 42 to 150 m above sea level (Adamo et al., 2003). Being an inter-mountainous area, the Solofrana valley is surrounded by high slopes and is characterized by the presence of both detrital–alluvial sediments and the fall of pyroclastic material from Somma–Vesuvius. Volcanic soil material occurring on the mountains has been colluviated to the valley, forming very thick, fertile soils which show moderate to high andic properties (Terribile and Di Gennaro, 1996). Andosols have a high binding capacity for heavy metals (Tanneberg et al., 2001).

The Picentini Mountains constitute the *horst* extending 900 km^2. The reliefs of the Sarno and Lattari mountains constitute the western edge of the Picentini Mountains, made by the Triassic dolomite, from limestone and dolomitic limestone of the lower Jurassic-Cretaceous as well as from Cretaceous fractured and karstified limestone (De Pippo et al., 2006). In the study area are located some of the highest peaks of the Picentini Mountains, such as Mt. Terminio (1786 m a.s.l., the second highest mountain of the Picentini Regional Park), Mt. Avella (1598 m a.s.l., Partenio Regional Park) and Montevergine (1493 m a.s.l., Partenio Regional Park). A central depression in the Picentini Mountains, joining the valleys of the Calore Irpino and Tusciano rivers, divides the chain in two geologically different sectors: the western one, where rocks are predominantly dolostone, with an alpine character and a well-developed surface hydrography, and the eastern one, mostly made up of limestone and clayey overlays, and generally a less sharp landscape. Karst topography is widely present.

On the SE side of Mt. Montevergine Mountain there is the city of Avellino. Avellino is located in a deep structural depression, 20 km^2 wide, at the external border of the southern Apennines, that breaks the continuity of the calcareous chain, and that is filled with Pliocene deposits, and overlaid by Quaternary formations. The depression is bordered by the calcareous Picentini Mountains (E), Avella Mountains (W), Sarno Mountains (S), and by the prevailing clay hills, related to Irpine Units (N). The substrate of the city is made of Jurassic-Cretaceous carbonate sequences, related to the Picentini Mountains stratigraphic unit, derived from the Campania-Lucania Platform deformation (Albanese et al., 2007d). Complete upper Triassic-upper Cretaceous sections are well exposed in the Picentini Mountains and in the Sorrento Peninsula, indicative of a platform-interior environment (Patacca and Scandone, 2007). Through an unconformity boundary, follow flysh deposits from the upper Miocene, belonging to Irpinian Supersynthem (Castelvetere and Gorgoglione Flysh). They are composed of coarse-grained sandstone and polygenic conglomerates. These deposits outcrop into the western portion of the urban area, and make up the structure of the surrounding hills (Maresca et al., 2012). Other upper Miocene–lower Pliocene deposits (Altavilla Unit) outcrop in the eastern part of Avellino, consisting of grey–blue clay and sand–gravel intercalations. The raising of the area during Upper-Pliocene, leads to erosional and depositional processes. The Pliocene clastic deposits (Avellino conglomerates) are made of the dismantled Ariano-Irpino Flysh. The conglomerates are made up of polygenic pebble cemented (puddingstone) into a clayey matrix that forms strata or lenses; these have built up the hills to the eastern part of Avellino (Maresca et al., 2012). The Avellino depression is filled by the products of the Ignimbrite Campana formation (39000 y.a.), a strong Phlegrean eruption that affected most of the Campanian area. Other pyroclastic deposits (e.g. the Ottaviano, Pollena and Avellino formations) cover all these previous geological units, together with Quaternary alluvial sediments.

3.2.2. Climate and hydrography

The climate is Mediterranean, with variations from the coastline, with mild winter and not rainy, hot summer (temperatures > 35°C), to the inner mountainous areas with temperate summer (rarely higher than 30°C) and cold winter (reaching also -10°C).

The highly permeable calcareous formations of the Picentini Mountains produce the most productive aquifers in the central sector of Campania, where the average rainfall reaches and sometimes exceeds 1500 mm per year (De Pippo et al., 2006). In the western sector of the study area flow the three watercourses feeding the Sarno River: the Solofrana Stream and the briefer Cavaiola Stream, which flow into the Nocerino artificial channel. The highest point of the western Picentini Mountain chain is Pizzo d'Alvano (1133 m a.s.l.), which feeds several springs still active at the foot of the Sarno limestone massif, close to the town of Sarno. The main springs (Santa Maria la Foce, Mercato, Palazzo and Santa Marina)

were used for feeding the Campanian aqueduct. A great variation in the nature of the springs' waters at a short distance exists. Many of these springs, in fact, show a local mineralization phenomena, due to the uprising of fluids along faults and fractures, passing through volcanic deposits (Del Prete et al., 2008). In the eastern sector of the area the Terminio Mount gives origin to Sabato River, tributary of the Calore Irpino River, feeding several significant springs (della Madonna, delle Acque Nere, di Serino) and the Alto Calore aqueduct. Feeding the Sabato River is the Fenestrelle Creek, which has been fundamental for the Avellino economy. Exploiting the water power of Fenestrelle Creek, a lot of mills and paper mills, wool processing and ironworks grew up along his shores. Today the Fenestrelle river is quite polluted, due to the urban discharge not sufficiently purified. The climate of Avellino, wet and rainy, causes frequently flood disaster as well, the last one verified in October 1985, with fortunately no population damages.
Along the coastline, the city of Salerno is part of the Sele River Plain.

3.2.3. Land use

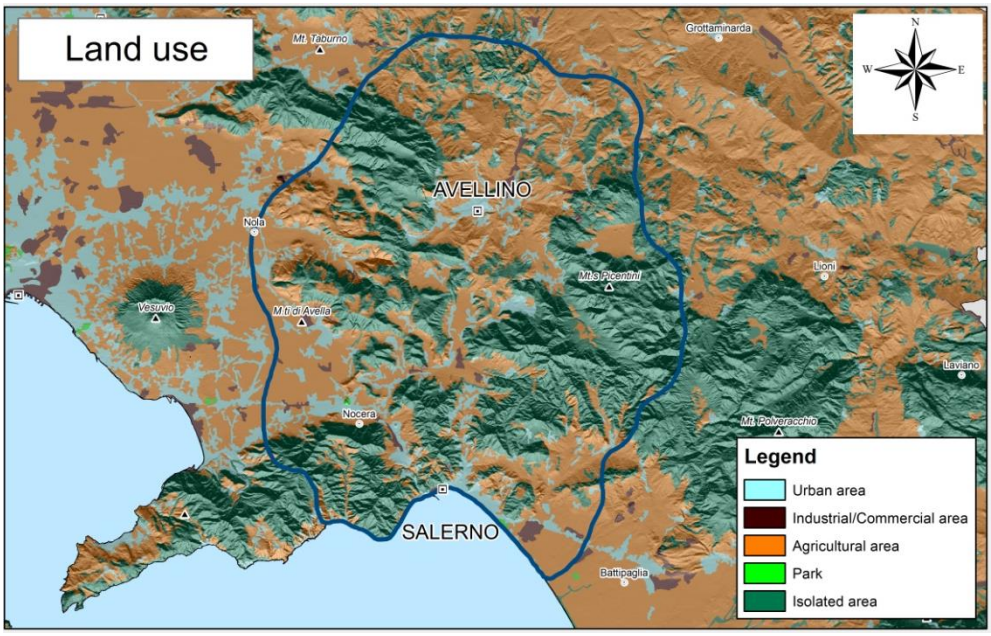


Fig. 3.6*: Land use map of the selected area (from Corine Land Cover 2012).*

Salerno is the second most populated Province in Campania after Napoli (1.106.506 inhabitants in 158 Municipalities and a density of 224 inhabitants/km^2); Avellino is the fourth one following Caserta and Benevento (425.325 inhabitants in 118 Municipalities and a density of 153 inhabitants/km^2). Other important urban areas are: Cava de' Tirreni (53.659 inhabitants), Nocera Superiore (24.263 inhabitants), Nocera Inferiore (46.266 inhabitants), Mercato San Severino (22.322 inhabitants).

The study area includes three protected areas of the eight Regional Parks: Picentini and Partenio Mountains, and Sarno River. The Partenio Mountains Regional Park has an extension of 16.650 ha. Its highest peak is represented by the Montevergine Mountain. The

Pincentini Mountain has an environmental and idrogeological significance, and is the wider Regional Park, extending between the Calore, Sabato and Sele Rivers on a surface of 630 km^2.

In the inter-mountainous areas, where the slopes are lower and the soils fertile for the for the presence of volcanic material, the agriculture activity is very intensive. In particular :

- Avellino is an agricultural city, and the tradition continues still nowadays. The 40.3% of the land in Avellino Province is used for agricultural purpose, especially for tobacco, viticulture and the production of hazelnuts;
- in the Solofrana valley, mainly consisting of field horticulture, orchards and greenhouse horticulture and floriculture. On the southern slope land use generally consists in terraces with coexisting horticulture, fruit trees and vineyards, while chestnuts are widely grown on the north-facing slopes (Adamo et al., 2003).

The Solofrana valley is an area of considerable industrial activity. A total of 160 tanning plants operate in the upper Solofrana valley, between Solofra, Mercato S. Severino and Fisciano (Arienzo et al. 2001). In the past, industrial activity contributed with their Cr-containing effluents to the Cr-enrichment of the Solofrana river waters (Basile et al., 1985). In recent years, the concentration of Cr in river water has decreased as a result of improved wastewater control from the tanning plants (Adamo et al., 2003), while stream sediments (De Vivo et al., 2003) and soil still have Cr and other trace elements concentrations higher than the natural *background* values (Adamo et al., 2003). The waters flow into the Sarno river, which is considered the most polluted water course in Campania although contamination level has not been well documented since 1975 (Basile etal., 1985). In the middle Sarno valley, between Sarno, Nocera Inferiore, and Scafati, agriculture is intensive. Tomato (Lycopersicon lycopersicon L., CV San Marzano) is the principal row crop and extends over 3500 ha. The basin is characterized by the presence of 183 tomato plants. The river is also affected by non point sources of pollution including fertilizers from farm effluents, and receives wastes from dairy, paper-mill and the pottery industries (Arienzo et al., 2001).

In Avellino the manufacturing sector plays an important role, with an industrial zones on the north-eastern peripheries of the main urban area, at Pratola Serra. Many small and medium-sized businesses are located in the industrial zones, including notably FMA (Fabbrica Motori Avellino/*Avellino Engine Factory*) who produces engines for Fiat, Opel, Lancia and Alfa Romeo, and creator of the "multi-jet" (fuel injected) car engine.

Industry has not the leading role in the economy of Salerno. Numerous companies, that constitute a fifth of the Campanian companies, are still active (22% manufacturing, pottery,

food production and treatment, 23% constructions), although the economy of Salerno is mainly based on services industries, as most of the city's manufacturing base did not survive the economic crisis of the 1970s. During the last years, Salerno tried to grow up as a tourist city, facilitated because it is an important junction for the railway, marine and road transports; is located on the Napoli/Salerno and Salerno/Reggio Calabria highways; the railway is part of the high velocity line Roma - Salerno, and is connected with Reggio Calabria, and Potenza-Taranto; the port is one of the most active of the Tyrrhenian Sea, handling about 10 million tons of cargo per year, 60% of which is made up by containers.

3.3 Sampling sites, analysis and elaboration

Before collecting the samples, a grid with cells of 4 km^2, covering an area of 220 km^2, has been constructed by means of GoogleEarth software. A total of 102 samples (Fig. 3.7) has been collected and analyzed with the same procedures explained in Chapters 1.3 and 1.4. The survey was carried out during spring-summer 2015 and in the geochemical laboratories of the University of Naples the sample preparation, in particular the drying, the disaggregation and sieving phases, took place (Fig. 3.8).

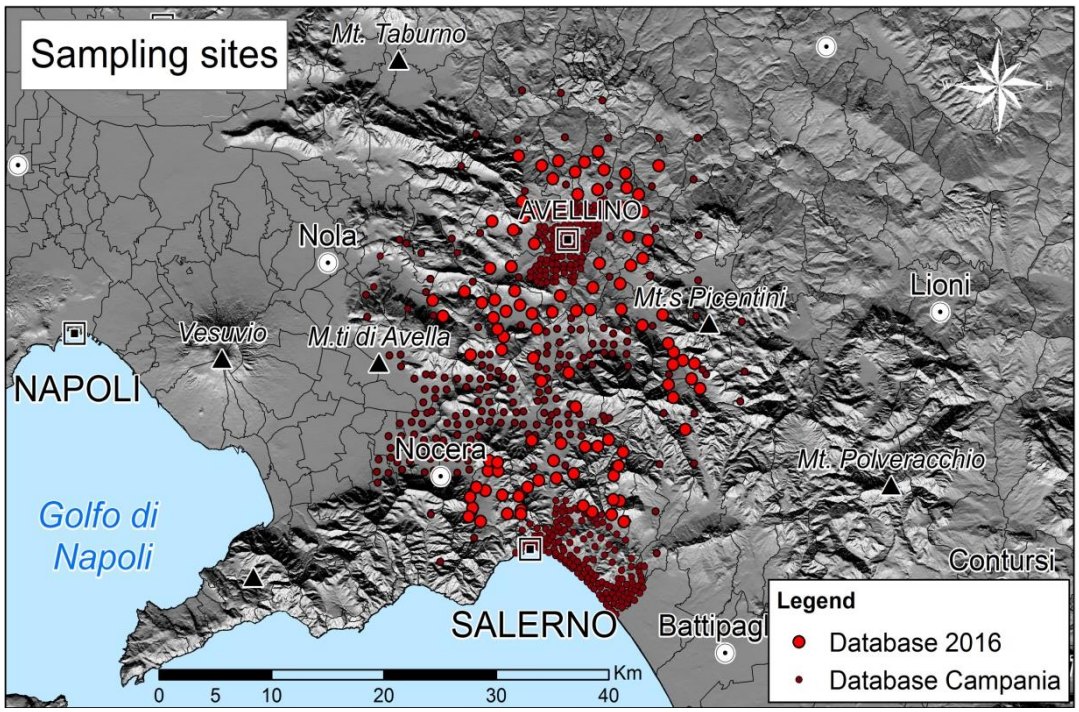


Fig. 3.7*: Sampling grid and sites of the selected area.*

The analysis were again conducted in the Bureau Veritas Analytical Laboratories Ltd. (Vancouver, Canada), where they determined by a combination of ICP-MS (inductively coupled plasma mass spectrometry) and ICP-AES (Inductively coupled plasma atomic emission spectroscopy), following a hot aqua regia digestion, the concentrations of 53 elements: Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In,

K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V,W, Y, Zn and Zr.

Fig. 3.8:*Example of sampling and sample preparation at the University of Naples Federico II.*

The 102 new samples were then added to the old database in order to obtain a major density of the samples in the area. The final database have a total number of 584 samples.

3.4 Statistic and cartographic elaborations

R software was used for graphical data analysis. In particular were elaborated:

- Summary tables of the results (minimum, maximum, mean, median, 1st and 3rd quantiles, Table 3.1);
- Cumulative probability (CP) plots in log scale, where: the black line represents a straight line forcing the data points, that can be useful to visualize the data trend; the vertical red line represents the CSC threshold limit;
- EDA plot, a combination of several graphics (histogram, density function, one dimensional scatter plot and box plot) in log scale, to detect most aspects of the data distribution.

Dot maps, interpolated maps, *background/baseline* maps and the CSC intervention threshold values maps were elaborated for the 15 potentially toxic elements listed by the

D.Lgs152/06 (see Chapter 1.6 for the description of the method). In this chapter follows the description of the maps.

Table 3.1*: Main statistical parameters(number of samples, minimum, maximum, first quartile, third quartile, mean, median) for the Avellino-Salerno area.*

Element	Units of measure	Samples number	Minimum value	1st Quartile	3d Quartile	Maximum value	Mean	Median
Al	%	583	0.660	4.07	6.39	9.47	5.12	5.50
Ca	%	583	0.220	1.58	4.72	20.7	3.76	2.33
Fe	%	583	0.390	2.48	3.27	4.70	2.83	2.91
K	%	583	0.110	0.620	1.96	4.76	1.46	1.24
Mg	%	583	0.260	0.640	1.31	7.49	1.28	0.790
Na	%	583	0.002	0.100	0.391	1.27	0.318	0.240
P	%	583	0.020	0.106	0.233	0.870	0.180	0.160
S	%	583	<0.02	0.030	0.060	0.310	0.047	0.040
Ti	%	583	0.004	0.111	0.175	0.327	0.142	0.150
Ag	µg/kg	583	<2.0	59.0	124	2286	123	85.0
As	mg/kg	583	2.80	11.1	19.1	112	15.4	14.4
Au	µg/kg	583	<0.2	2.40	7.80	915	13.5	4.00
B	mg/kg	583	3.00	10.0	19.0	98.0	15.6	14.0
Ba	mg/kg	583	38.0	355	663	1143	509	519
Be	mg/kg	456	0.500	4.10	7.40	16.9	5.73	5.50
Bi	mg/kg	583	0.040	0.350	0.560	0.970	0.455	0.460
Cd	mg/kg	583	0.080	0.310	0.560	2.33	0.460	0.400
Ce	mg/kg	305	12.1	76.0	114	194	96.6	92.7
Co	mg/kg	583	1.40	9.10	13.5	22.8	11.1	11.3
Cr	mg/kg	583	2.10	12.4	18.6	808	20.7	14.9
Cs	mg/kg	305	1.16	12.1	16.4	34.2	13.9	14.4
Cu	mg/kg	583	6.37	49.2	153	1556	128	85.1
Ga	mg/kg	583	1.40	8.15	13.2	21.3	10.4	10.5
Ge	mg/kg	305	0.050	0.100	0.200	0.400	0.119	0.100
Hf	mg/kg	305	<0.02	0.060	0.600	3.82	0.554	0.390
Hg	µg/kg	583	<5.0	39.0	88.0	922	82.4	58.0
In	mg/kg	305	0.010	0.020	0.040	0.120	0.034	0.030
La	mg/kg	583	4.40	37.2	60.8	144	48.0	48.2
Li	mg/kg	305	2.60	18.0	29.0	61.2	24.1	23.8
Mn	mg/kg	583	79.0	724	1055	3130	877	867
Mo	mg/kg	583	0.380	1.34	2.01	20.2	1.86	1.59
Nb	mg/kg	305	0.540	6.24	12.6	22.8	9.41	8.90
Ni	mg/kg	583	3.80	13.4	17.4	73.6	16.4	15.3
Pb	mg/kg	583	8.32	45.5	84.2	1306	82.4	61.2
Pt	µg/kg	305	1.00	1.00	3.00	45.0	2.62	1.00
Rb	mg/kg	305	21.6	97.8	184	254	140	133
Re	µg/kg	305	0.500	0.500	1.00	7.00	0.954	1.00
Sb	mg/kg	583	0.140	0.460	1.10	20.0	1.18	0.670
Sc	mg/kg	583	0.300	2.20	3.30	9.60	2.86	2.70
Se	mg/kg	583	<0.1	0.400	0.700	1.50	0.523	0.500
Sn	mg/kg	456	0.300	2.80	4.90	126	4.790	3.800
Sr	mg/kg	583	23.3	122	229	510	187	175
Te	mg/kg	583	<0.02	0.010	0.050	0.150	0.034	0.030
Th	mg/kg	583	0.800	10.3	18.6	47.8	14.8	14.3
Tl	mg/kg	583	0.130	1.19	2.08	3.05	1.61	1.74
U	mg/kg	583	0.500	2.60	6.50	23.7	4.93	4.70
V	mg/kg	583	14.0	65.0	98.0	138	79.7	82.0
W	mg/kg	583	0.050	0.900	1.70	6.50	1.31	1.30
Y	mg/kg	305	1.95	13.8	21.7	64.4	18.0	16.4
Zn	mg/kg	583	17.9	81.9	147	1682	136	101
Zr	mg/kg	305	3.30	24.5	55.3	270	48.2	35.1

3.4.1 Description of the potentially toxic elements with values above the CSC threshold limits

3.4.1.1 Arsenic (As)

Arsenic content in the analyzed samples varies from 2.8 mg/kg to 111.5 mg/kg, with a median value of 15.3 mg/kg. The maximum values are quite lower than the Campanian values (0.6-164 mg/kg), but still higher than the Italian values (2.67-63 mg/kg). The European top soils show a wider concentration range (0.32-282 mg/g), but a lower median value (6 mg/kg) (De Vivo et al., 2008a, 2006).

Only 5% of the samples (95° percentile) have As concentrations >21 mg/kg; those are grouped in particular in Avellino city, but sparse values are distributed along the Solofrana valley and on the shores of Sabato river as well.

The interpolated map confirms that high As contents (> 24 mg/kg) are localized in some spots around Avellino city (Aiello del Sabato), in some areas on the Picentini Mountains, close to the Sabato river, and along the Solofrana valley. Here the highest values, between 41 amd 111 mg/kg, are concentrated, in particular in the Solofrana valley and in Bracigliano municipality. Those high values are probably due to anthropic activities. Intermediate concentrations (12-24 mg/kg) are well influenced by volcanic deposits; those values can be found on the calcareous mountains, and generally in all the areas characterized by a pyroclastic overlay. The remaining areas (Salerno city, some floodplain areas, and the clayey sandstone in the northern part of the study area) are characterized by low As contents (<24 mg/kg).

The *background/baseline* map confirms that the territory not influenced by volcanic sediments shows values <11 mg/kg. The majority of the territory, interested by a pyroclastic overlay, have values ranging between 13 and 35 mg/kg, compatibly with the natural *background* for volcanic soil. The high concentrations (35-46 mg/kg), influenced by anthropic activities, can be found only in two spots, one along the Solofrana valley (close to Mercato San Severino municipality) and one in Bracigliano municipality.

From the totality of the analyzed samples, 19.6% overcomes the CSC value for residential use (20 mg/kg), as established by the D.Lgs. 152/06, while only two samples overcome the CSC value for industrial/commercial use (50 mg/kg), corresponding to the highest values found in the *background/baseline* map. The overcoming for residential use is compatible with the *background* concentration values for volcanic soils. The occurrence of those values is in areas interested by a volcanic overlay, but known for uncontrolled anthropic activities.

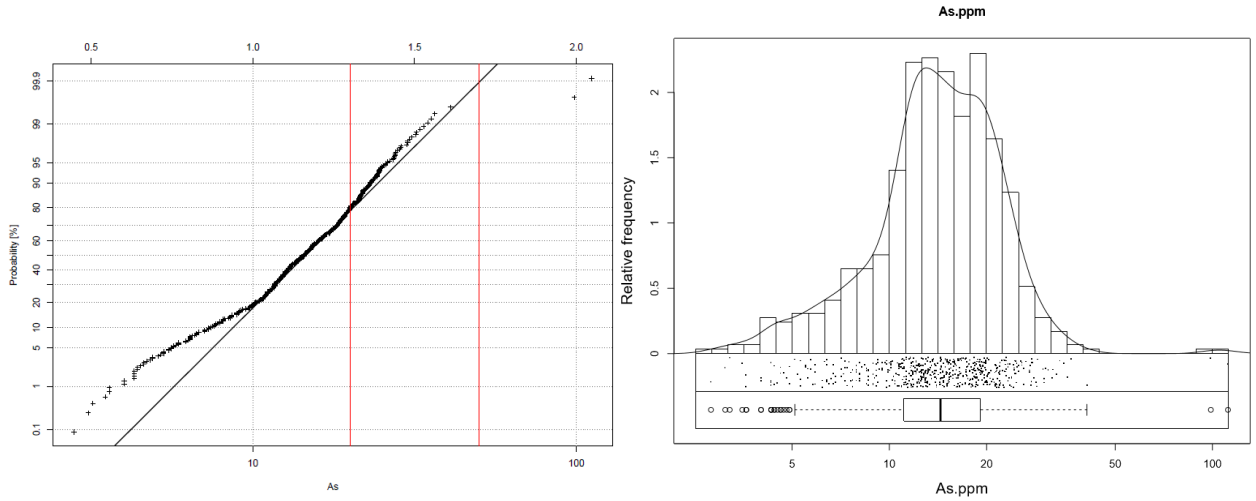


Fig. 3.9:*CP (on the left) and EDA (on the right) plots for As in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

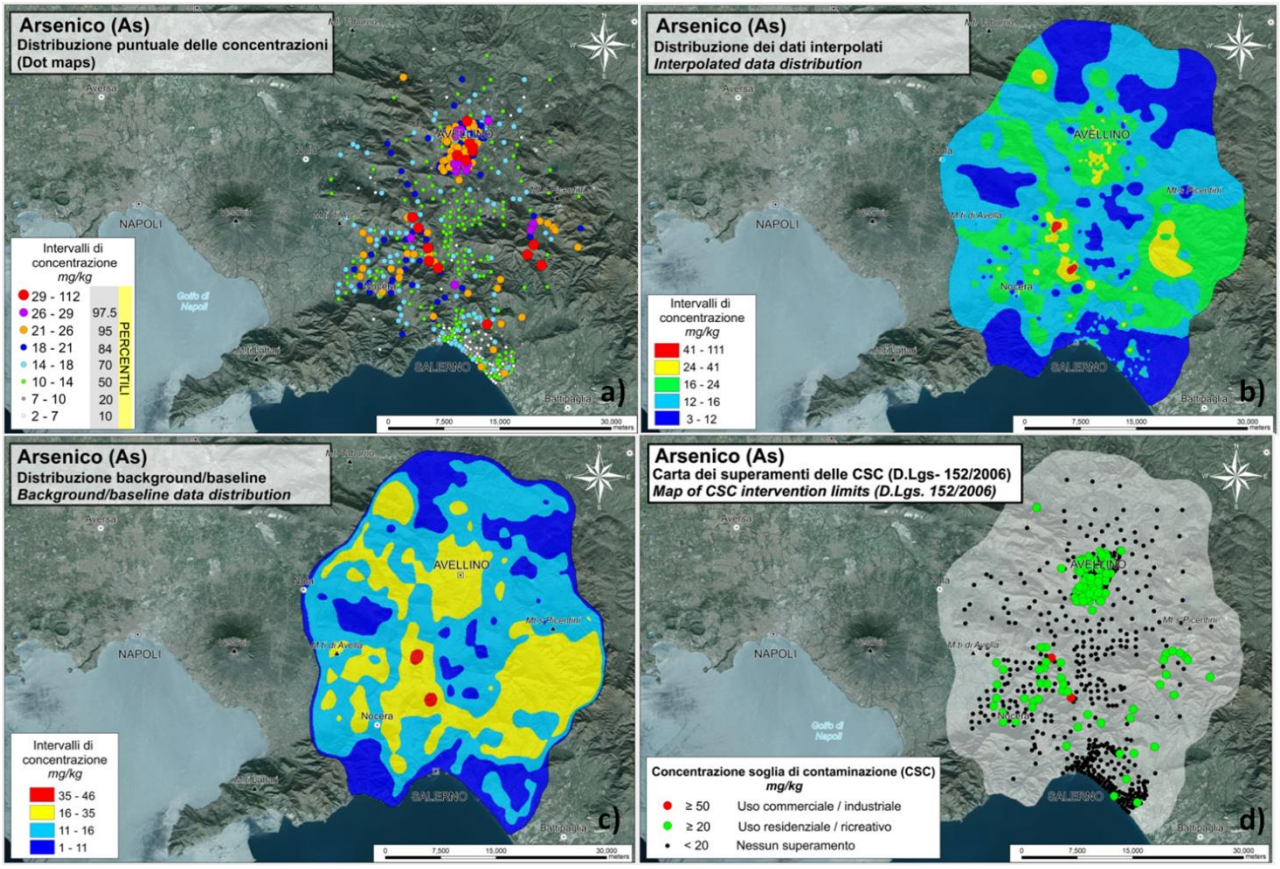


Fig. 3.10:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for As.*

3.4.1.2 Beryllium (Be)

The measured Be concentrations vary between 0.5 mg/kg to 16.9 mg/kg, similar to the Campanian values, with only the median value quite higher (5.5 mg/kg and 4.5 mg/kg respectively).

From the dot map is it possible to observe that only 10% of the samples have Be concentration >7.8 mg/kg. Those samples can be found sparsely in the Solofrana valley and Sarno river plain, in the area between Nocera Superiore and Cava de' Tirreni municipalities, and on the Picentini Mountains, in particular close to Sabato river valley.

In the interpolated map, the distributions are better highlighted; the lowest values (<4.6 mg/kg) are controlled by silico-clastic and carbonate lithologies, in the southern and northern parts of the area; Be concentrations between 4.6 mg/kg and 10.7 mg/kg are found in the soils forming from the pyroclastic overlays. Beryllium tends to concentrate in the late magmatic products, ejected in the pyroclastic *fall out* during explosive events, mainly characteristic of Somma-Vesuvio volcano.

Almost the 5% of the samples (95° percentile) have Be >10 mg/kg, representing the threshold value for soils designated to industrial/commercial use. These spotted areas are located in the eastern portion of the Sarno river plain, close to Sarno municipality, in the Solofra basin, close to Mercato San Severino municipality, in south of Avellino, in the Sabato river, and in a wide area in the southern Picentini Mountain.

The *background/baseline* map shows that the areas with Be values < 5 mg/kg correspond to silico-clastic lithologies. High values between 5 mg/kg and 12.3 mg/kg can be found in correspondence of pyroclastic overlays. The values between 7.5 mg/kg and 12.3 mg/kg are probably due to the outcropping of volcanic lithologies (trachyte, tefrite, latite, phonolite, basalt). Two spots with Be values >12.3 occur in the south of Avellino, and in the southern area of the Picentini mountains.

Almost all of the Be top soils values overcome the CSC values for residential use (2 mg/kg), and only the 10% of the samples is lower, while 5.7% of the samples exceed the CSC for industrial/commercial use (10 mg/kg). The thresholds established by the D.Lgs. 152/06 are probably too low, and do not take into account the natural *background* values, due to the volcanic occurrences in the area.

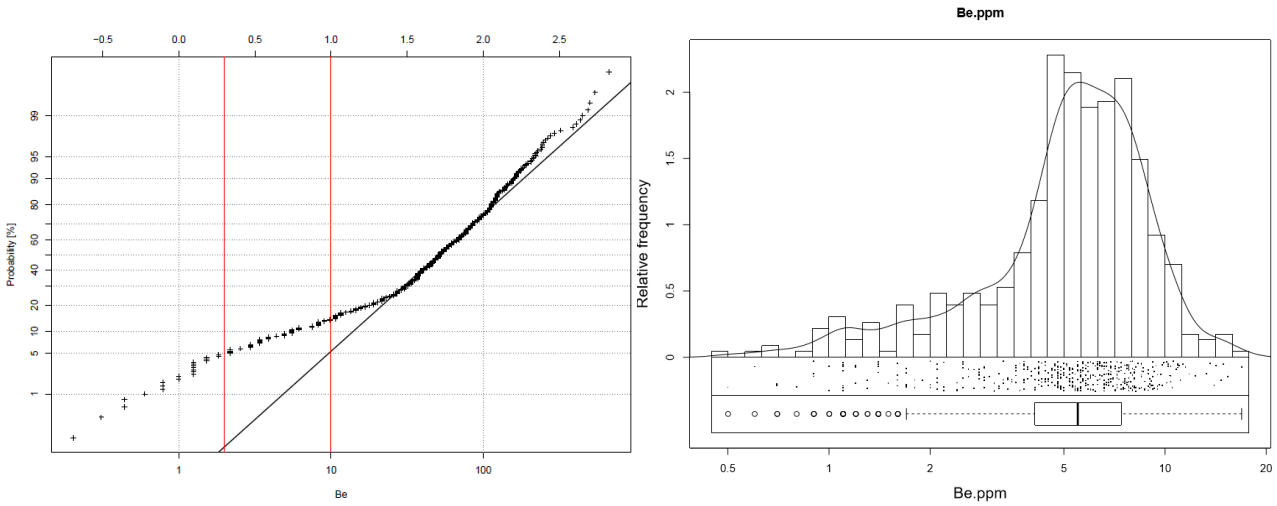


Fig. 3.11:*CP (on the left) and EDA (on the right) plots for Be in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

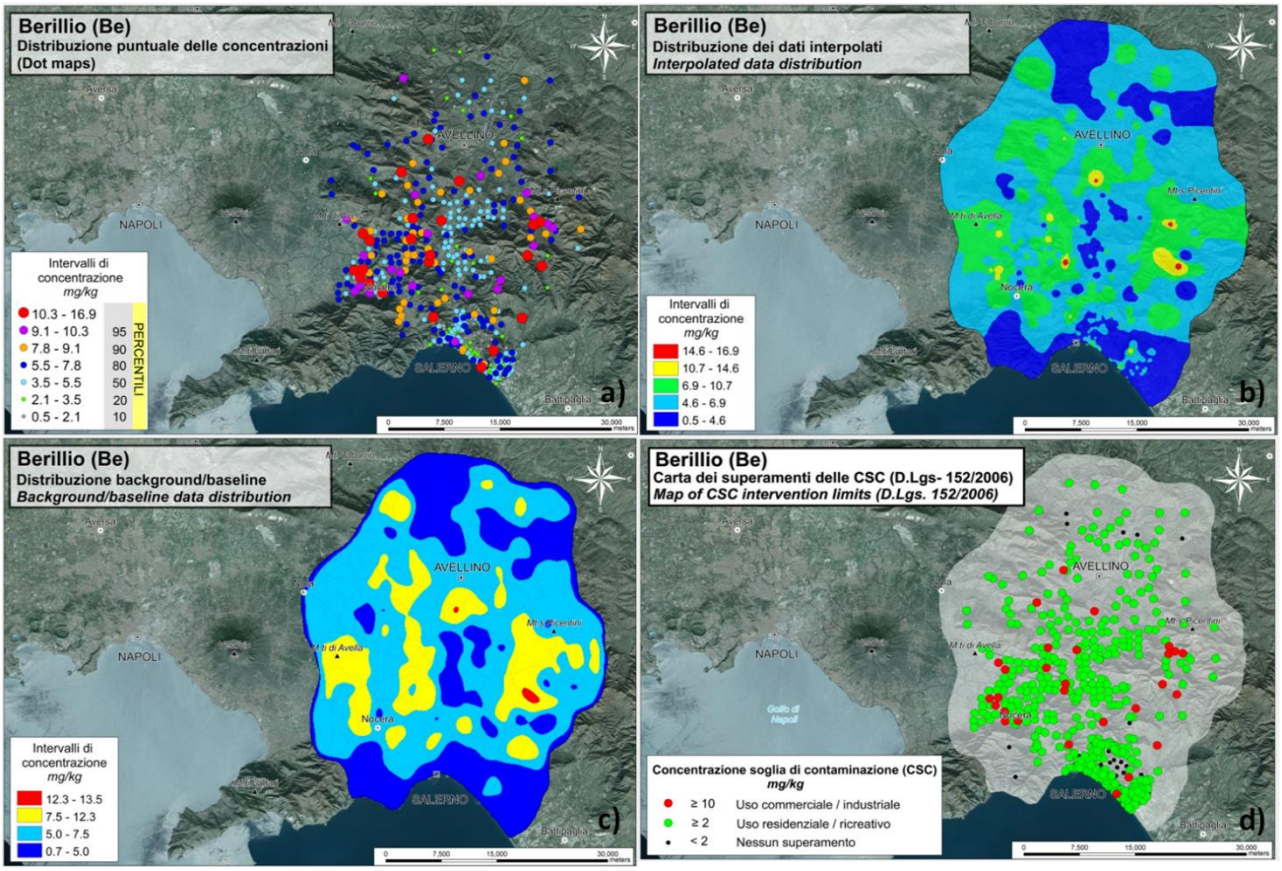


Fig. 3.12:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Be.*

3.4.1.3 Cadmium (Cd)

Cadmium content in the analyzed samples varies between 0.08 mg/kg to 2.33 mg/kg, much lower than the maximum value found in the Campanian top soils (11.06 mg/kg). The median value of 0.4 mg/kg is comparable with the Campanian one.

The dot map shows that only 2.5% of the samples (97.5° percentile) have Cd concentration >1.10 mg/kg. These samples are located in the Nocera municipality, Salerno and Sele plain, on the Picentini Mountains and in the Sabato river valley.

The interpolated distribution map shows that the majority of the territory has concentration <0.67 mg/kg. The lowest values <0.33 can be found in correspondence of silico-clastic lithologies. The high concentrations, >0.67 mg/kg, including the anomalies evidenced in the dot map, are located locally in Nocera, Salermo, Sele plain and in a wide area on the Picentini Mountains.

The *background/baseline* map shows that the northern and southern parts of the area, characterized by silico-clastic lithologies have Cd values <0.4 mg/kg. The remaining territory shows Cd values between 0.4 and 0.7, compatible with the *background/baseline* values found in Neapolitan and Salerno provinces (0.5-0.68 mg/kg, Cicchella et al., 2005; De Vivo et al., 2006). Small areas in Nocera and Salerno have concentrations between 0.7

and 1.2, and wide areas in the Picentini Mountains and in the north-western zone, have values >1.2 mg/kg.

There are no overcoming of the CSC value for industrial/commercial use (15 mg/kg), while only three sites overcomes the threshold for soils destined to residential/public use (2 mg/kg).

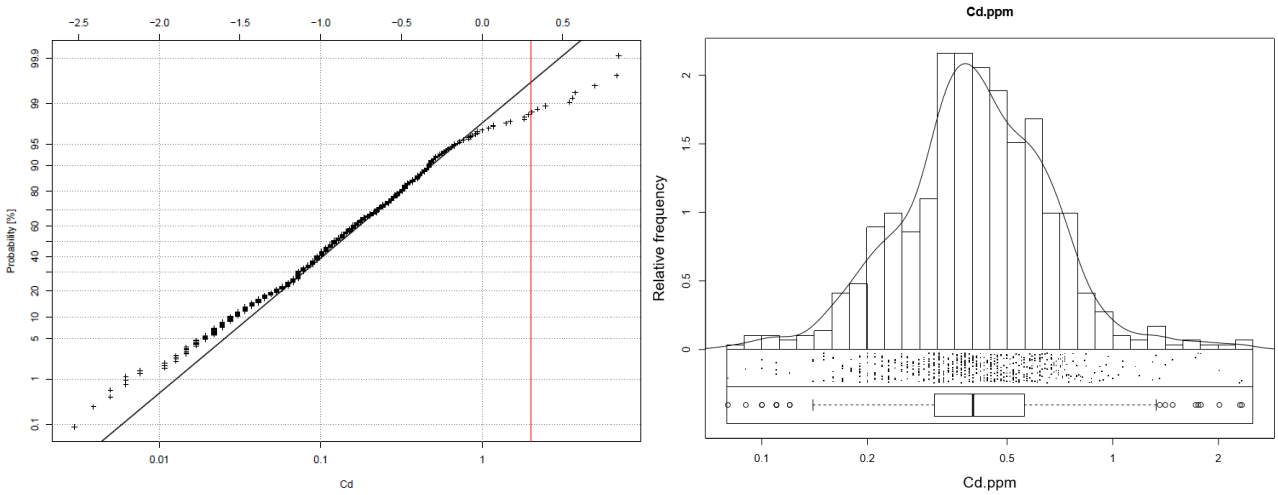


Fig. 3.13:*CP (on the left) and EDA (on the right) plots for Cd in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

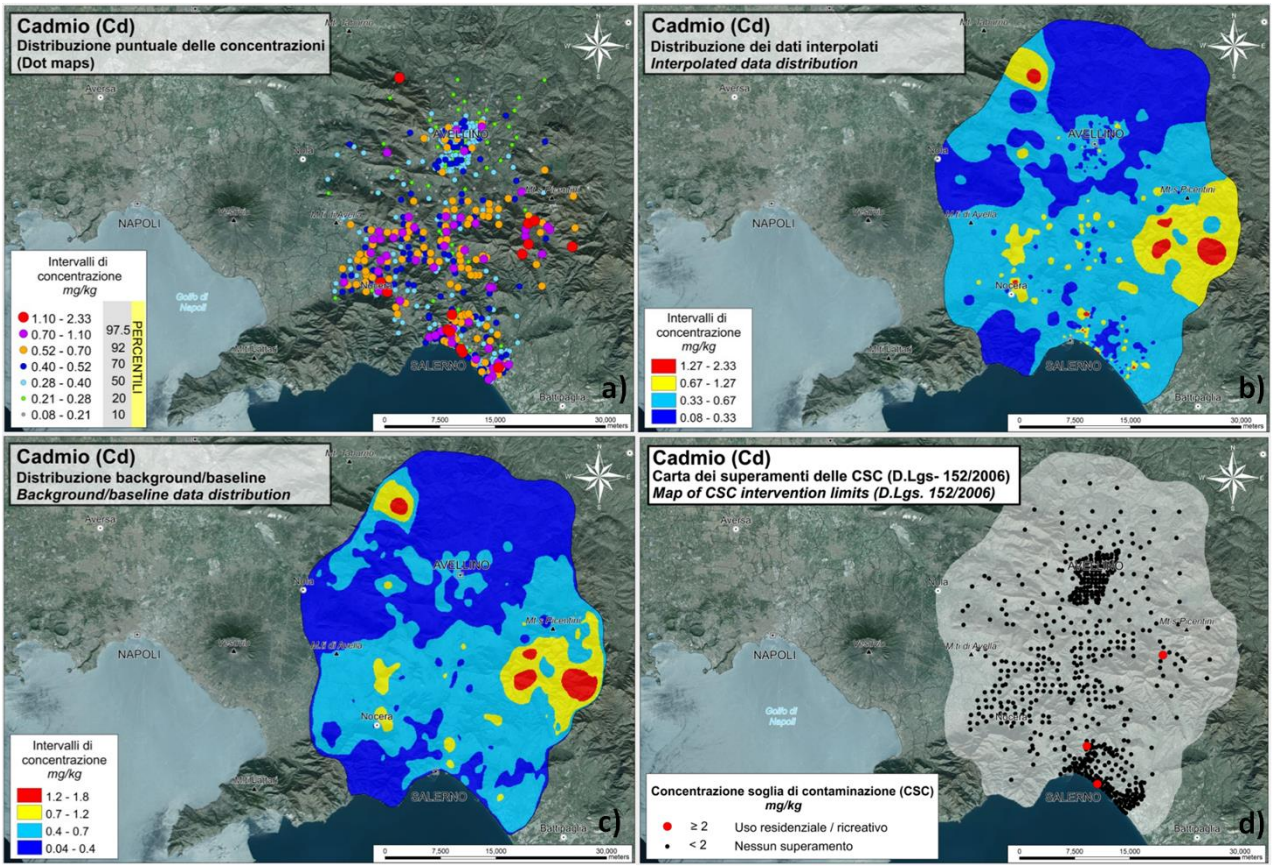


Fig. 3.14:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Cd.*

3.4.1.4 Chromium (Cr)

Chromium concentrations in the analyzed top soil samples are between 2.10 mg/kg and 808.4 mg/kg, with a median value of 14.9 mg/kg, the same values found in the Campanian top soils.

The dot distribution map shows that 97.5% of the measured soils have concentrations <41.4 mg/kg. The remaining 2.5% of the samples is located along the course of Solofrana basin, up to the Sarno plain. Some *hot spots* can be found also in the Sele plain in Avellino area.

The interpolated distribution map shows Cr concentrations <19 mg/kg in almost all the region. Intermediate values, between 19 and 67 mg/kg, are distributed in Sele and Sarno plains, and in the northern area characterized by silico-clastic deposits, where Cr contents is probably controlled by clay content. High *hot spots* (67-808 mg/kg) are located in the lower, and, especially, middle course of Solofrana river, probably controlled by anthropic contribute.

In the *background/baseline* map, almost all the area is characterized by values <16 mg/kg, and wide areas have concentrations <35 mg/kg. Those values are compatible with the natural *background* evaluated for neapolitan soils by Cicchella et al. (2005) and for salernitan soils by De Vivo et al. (2008). Higher values can be found in the Sele plain, and in particular, with the highest values, from Bracigliano to the Solofrana river valley, which concentrations have already been explained with an anthropic contribute (Albanese et al., 2012 e 2015; Adamo et al., 2015).

Only 4 sites overcome the CSC threshold value for residential/public use (150 mg/kg), and only one, in Bracigliano, overcomes the CSC for industrial/commercial use (800 mg/kg).

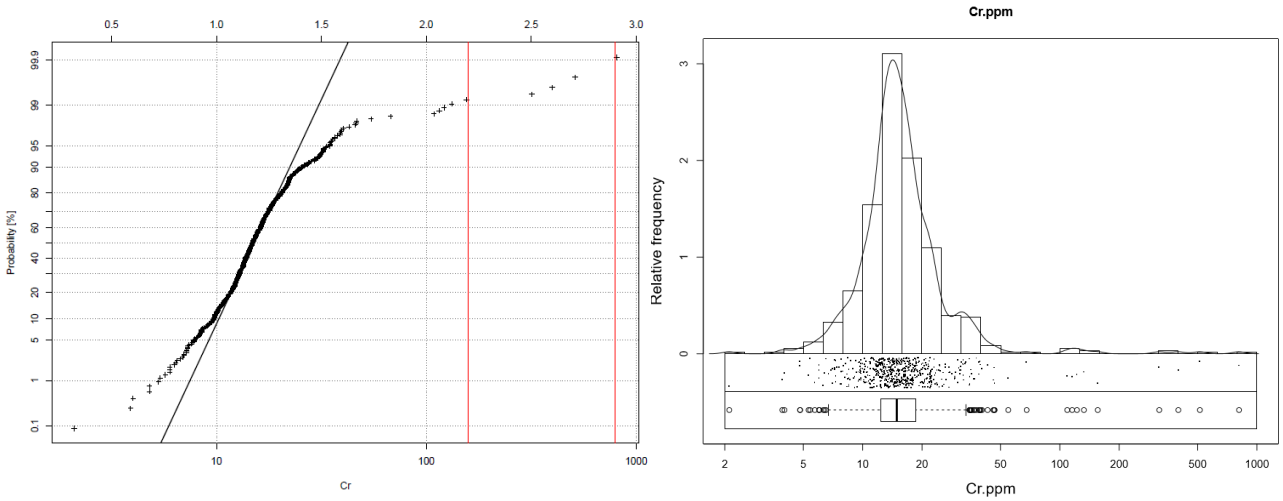


Fig. 3.15:*CP (on the left) and EDA (on the right) plots for Cr in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

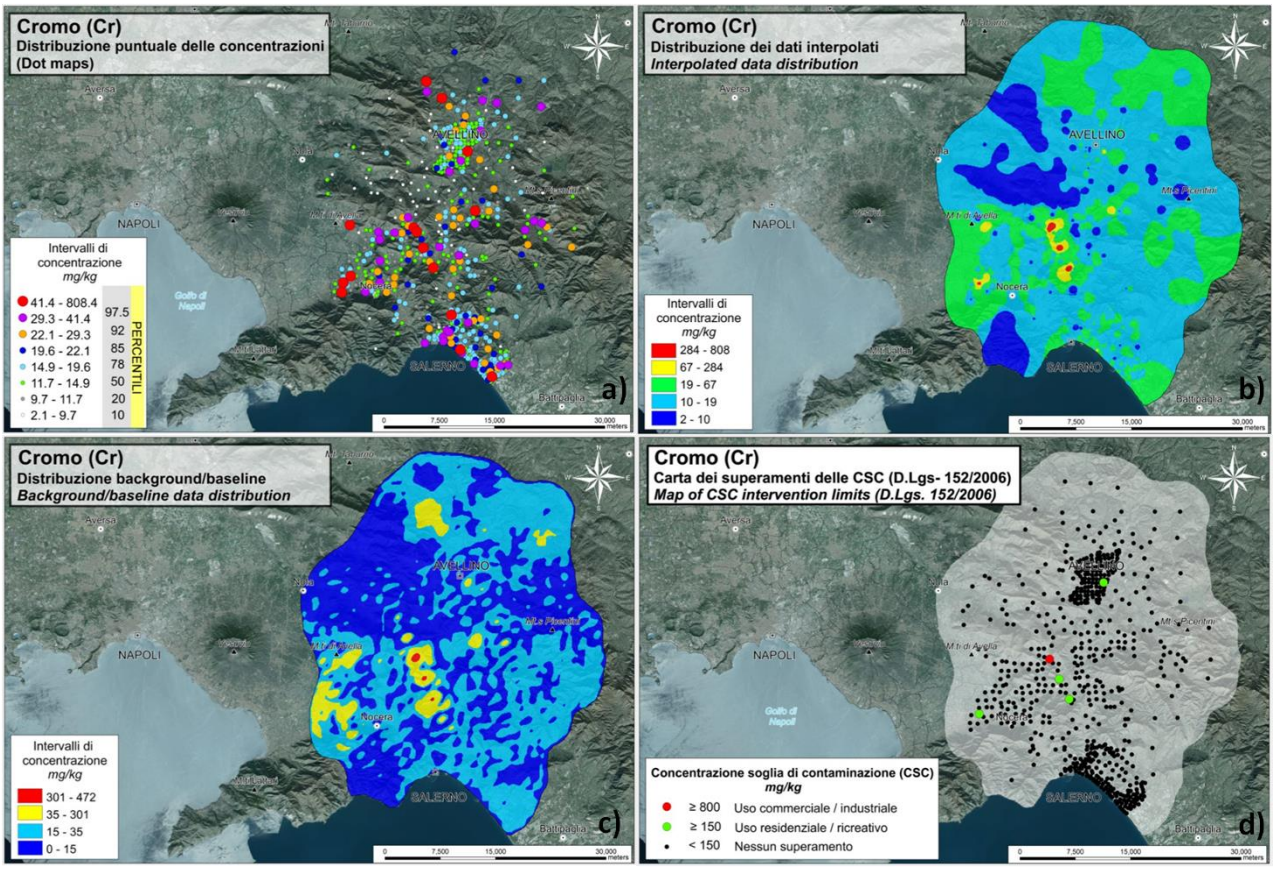


Fig. 3.16:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Cr.*

3.4.1.5 Copper (Cu)

The concentrations in the analyzed top soil samples are between 6.37 mg/kg and 1555.87 mg/kg, quite lower than the Campanian maximum value (2395 mg/kg), but with a higher median value (85.07 and 63 mg/kg respectively).

The dot map distribution shows that only 2% of the analyzed samples have Cu concentrations >347 mg/kg. Those sites are grouped in the eastern Sele plain, at the connection with the Solofrana basin. The 10% of the samples have Cu values >131, that are dispersed from Avellino to Mercato San Severino, to Solofrana basin.

The interpolated map shows that almost all the areas have Cu concentrations <177 mg/kg. Values >177 mg/kg are distributed around Avellino (Manocalzati, Aiello del Sabato), Solofra, Mercato San Severino, and from Nocera to Siano and Sarno plain. In these areas are included sites that overcomes 425 mg/kg. Some *hot spots* in the north-eastern part of Avellino, and in the area between Sarno and Nocera municipalities, Cu concentrations are probably influences by industrial and agricultural activities, reaching values between 1029 and 1556 mg/kg.

The *background/baseline* shows quite elevated Cu values. Only the mountainous areas (Lattari Mountains, Picentini Mountains, and Partenio Mountains) are characterized by low values <69 mg/kg. All the area from Avellino, to Mercato San Severino, Solofra river

valley, and Sele plain has high values, between 69 and 455 mg/kg, related to the intense agricultural activities and to the presence in the territory of 160 tanning plants. In particular in the Sarno plain, between Sarno and Nocera, the background values are particulary high, (> 718 mg/kg).

Copper reveals an overcoming of the intervention limits (CSC), established by the law D.L. 152/06, for the residential use in 93.3% of the analyzed samples, and for industrial use top soils in 1.5% of the analyzed samples. The top soils with Cu concentrations above 120 mg/kg (CSC for residential use) are distributed from Avellino, to Mercato San Severino and Solofrana basin. In the Sarno plain are concentrated the top soils overcoming the industrial use intervention limit (600 mg/kg).

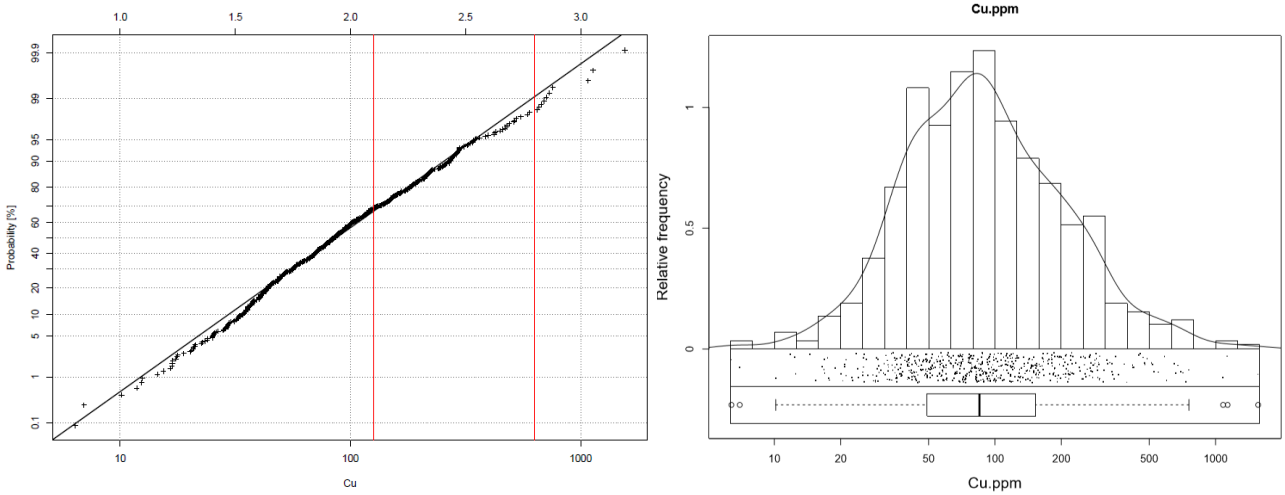


Fig. 3.17:*CP (on the left) and EDA (on the right) plots for Cu in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

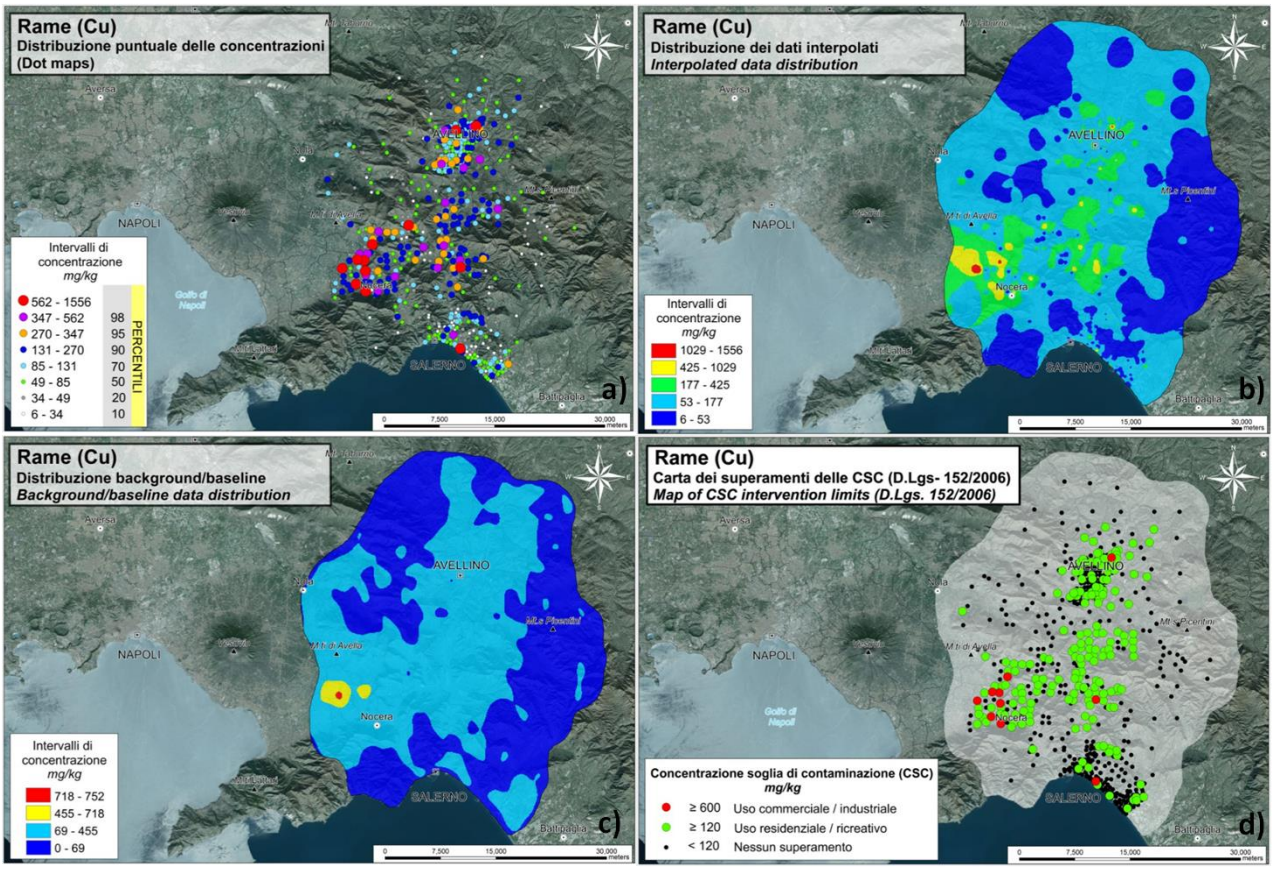


Fig. 3.18:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Cu.*

3.4.1.6 Lead (Pb)

In the analyzed top soil samples, the contents of Pb are between 8.3 mg/kg and 1306 mg/kg, quite below the Pb contents in the Campanian top soils (maximum value 2053 mg/kg), but with a similar median value (61 and 54 mg/kg respectively).

In the dot map, we can observe that 88% of the samples have Pb concentrations <112 mg/kg, and only 2% of the samples have concentrations >365 mg/kg. These highest values are concentrated in Salerno and Sele plain. Also the samples with Pb contents between 112 and 365 mg/kg are located especially in Salerno and Avellino, and some site can be found in Solofra municipality.

In the interpolated map, the highest values, >114 mg/kg and locally >333 mg/kg, can be found exclusively in Salerno city and Sele plain, and locally in Solofra; another small area is on the Avella Mountain. Intermediate Pb values, between 60 and 114 mg/kg, are located in the urban areas of Avellino, Cava de' Tirreni, Nocera, Sarno plain, Siano and Bracigliano, and in a wide area on the Picentini Mountains. The lowest values, <34 mg/kg, are located in the northern area, in correspondence of the clayey deposits

The *background/baseline* distribution map shows that the lowest background values are located in the northern part of the area, and on the Lattari Mountains, compatible with the geolitogenic characteristics of these zones. The remaining territory is characterized by

intermediate values, between 35 and 100 mg/kg, in accordance with the background values evaluated for the Campania region. Only Salerno, Sele plain and Solofra, and some small areas in Avellino, on the Picentini and Avella Mountains have background values >100 mg/kg and locally >541 mg/kg.

In the maps of the CSC intervention limits, we can observe that only one sample, in the north of Salerno, overcomes the CSC limit for the soils destined to industrial/commercial use (1000 mg/kg), while 14.9% of the analyzed samples exceeds the CSC limit for residential use (100 mg/kg). These samples are located especially in Avellino and Salerno cities, the most anthropic areas of the region. According to previous works (Cicchella et al., 2005), the high concentrations in the urban areas (especially in the neapolitan area where the measured contents are above 100 mg/kg) are due to the lead-base fuels used until '90, and, because of the characteristic of lead to being persistent, the soils in these areas will keep high concentrations until a new reclamation.

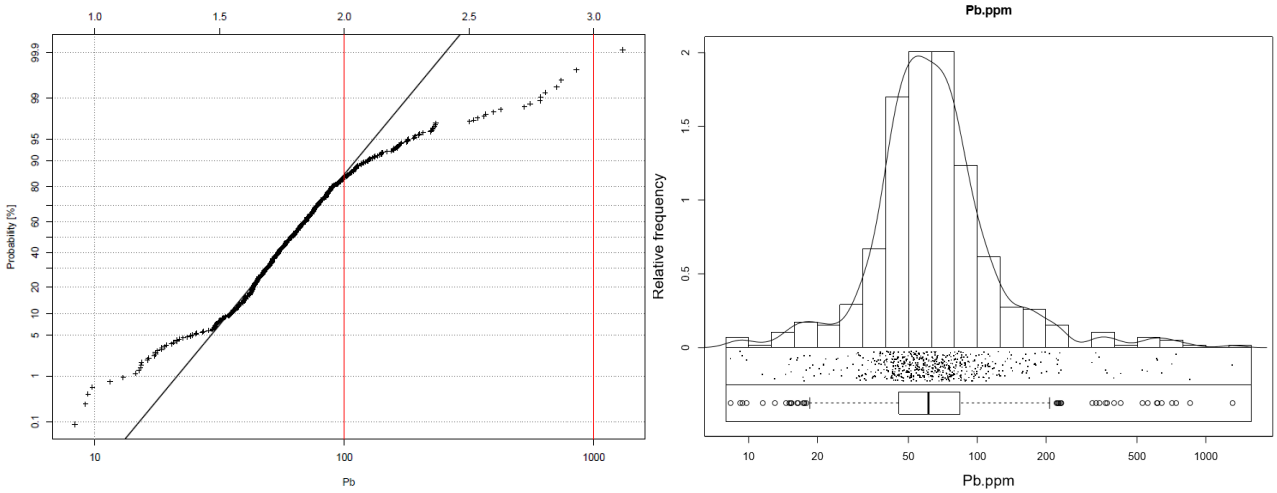


Fig. 3.19:*CP (on the left) and EDA (on the right) plots for Pb in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

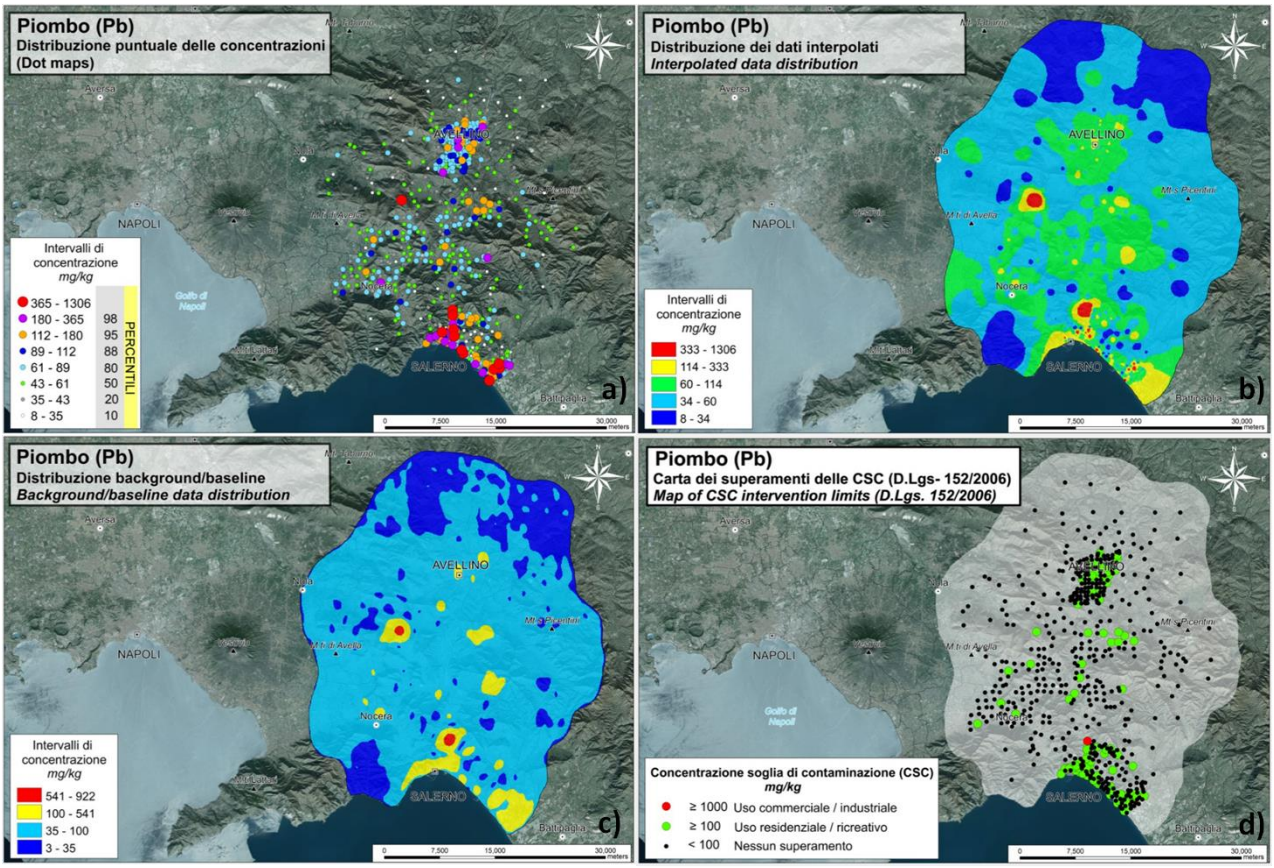


Fig. 3.20:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Pb.*

3.4.1.7 Antimony (Sb)

The Sb concentrations in the analyzed top soil samples vary between 0.14 and 20 mg/kg, quite below the maximum Campanian value (43 mg/kg), but with the same median value of 0.67 mg/kg.

In the dot map is it possible to see that 90% of the sampled sites have Sb concentrations <2.1 mg/kg, similar to the Italian values, and 2.5% of the samples have concentration >5 mg/kg. These sites are mostly located in Salerno city and Sele plain.

The interpolated map evidences that most of the area has Sb concentrations <0.7 mg/kg. Intermediate values (0.7-1.1 mg/kg) can be found around the urban areas and on the Picentini Mountains. High values (1.1-15.3 mg/kg) are limited to the main urban areas: Salerno, Cava de' Tirreni, Sele plain, Avellino, Mercato San Severino, Siano, Bracigliano, Nocera and Sarno. The only main area with the highest values, >15.3 mg/kg, is between Bracigliano and Lauro municipalities.

The *background/baseline* map displays two areas; one with values <0.5 mg/kg including the northern and south-western part, characterized by silico-clastic lithologies; one in Avellino and the central part, probably most controlled by volcanic deposits, with intermediate values (2.8-15.6 mg/kg); small areas in Salerno, Sele plain, Nocera, north

Bracigliano, are characterized by highest values (>15.6 mg/kg), probably with high anthropic impact.

Only 5 samples shows an surpassing of the CSC threshold values for residential/public use (10 mg/kg), while there are no overcoming of the threshold values for industrial/commercial use (30 mg/kg).

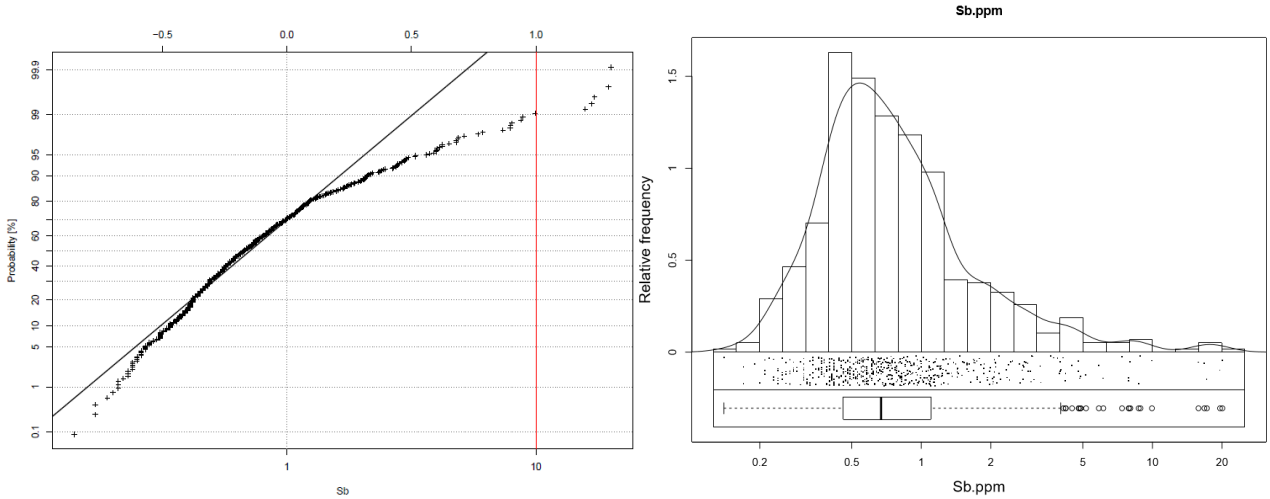


Fig. 3.21:*CP (on the left) and EDA (on the right) plots for Sb in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

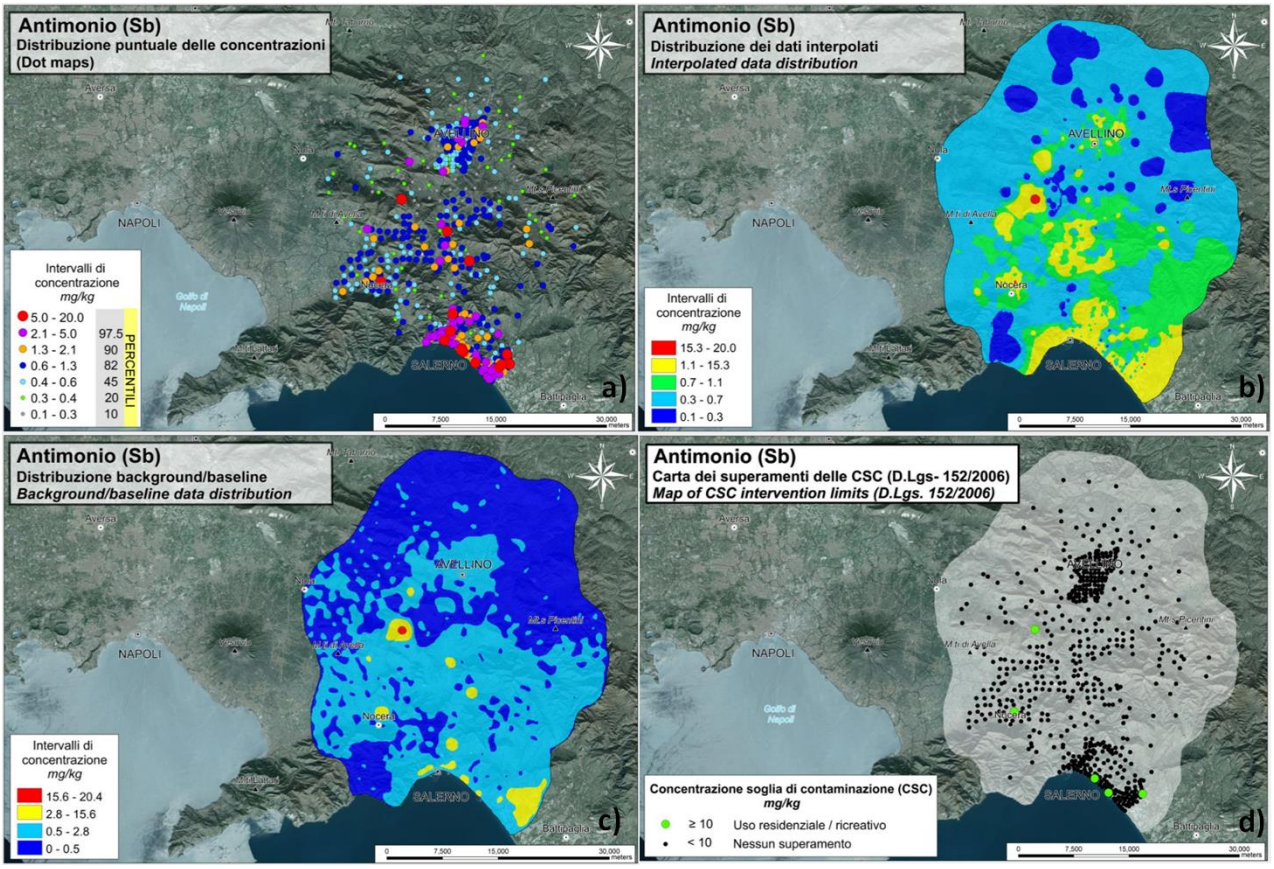


Fig. 3.22:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Sb.*

3.4.1.8 Tin (Sn)

Tin concentrations in the analyzed soils varies in the same range of Campanian top soils, from 0.3 and 126 mg/kg, with a slowly different median value (3.8 and 3.3 mg/kg respectively).

The dot distribution map shows that only 5% of the analyzed samples have Sn concentratiosn >10.7 mg/kg. Those samples are located in Solofra basin, Cava de' Tirreni, and especially Salerno and Sele plains. The northern part of the area has the lowest concentrations, <3.8 mg/kg.

The interpolated map confirms that the lowest Sn contents, <1.5 mg/kg, are located in the northern part of the area, interested by clayey deposits, and on the Lattari Mountains. Most of the area has Sn concentrations < 4 mg/kg. Higher concentrations (4-23.9 mg/kg) can be found along the urban areas of Salerno, Sele Plain, cava de' Tirreni, Nocera and Sarno Plain, Bracigliano, Siano, Mercato San Severino and Solofra (generally the Solofrana basin). Some high *hot spots* (>23.9 mg/kg) are located in Salerno city.

In the *background/baseline* map is it possible to observe that most of the area has values <6.6 mg/kg, with the lowest (<2.1 mg/kg) located in the northern area and on the Lattari Mountains. Some small zones (Salerno, Cava de' Tirreni, Sele Plain, Solofra and Nocera) shows the highest contents (6.6-29.2 mg/kg) with an anthropic contribute (illegal spills) that cannot be excluded.

Almost all the sampled sites show an overcoming of the CSC threshold values established by the D.Lgs. 152/06 for residential/public sites (1 mg/kg), while there are no overruns of the threshold for industrial/commercial use. Is evident that the CSC for residential/public use is not appropriate and should be modified with a major attention to the natural background.

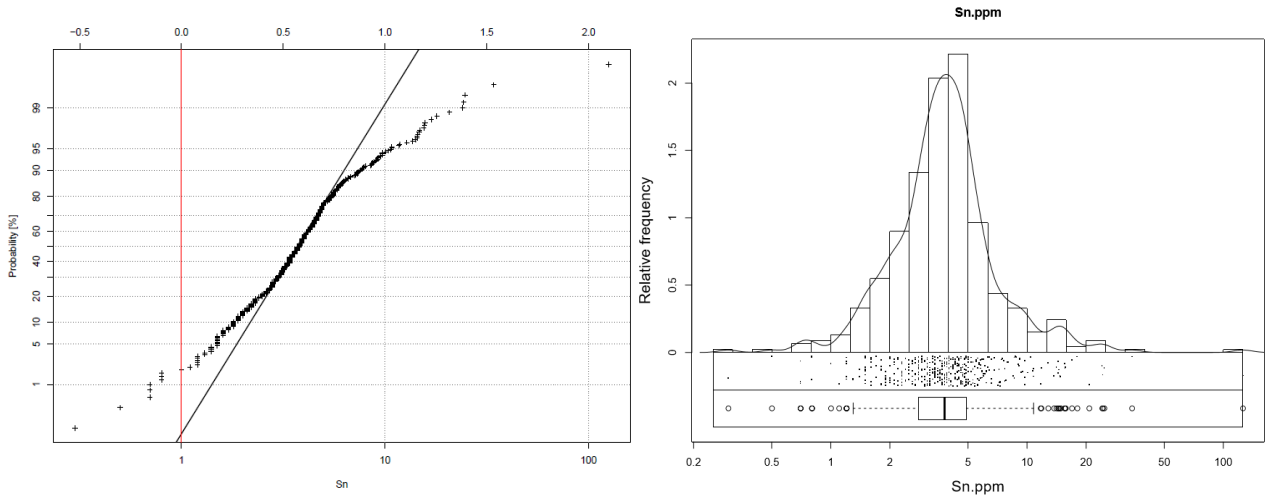


Fig. 3.23:*CP (on the left) and EDA (on the right) plots for Sn in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

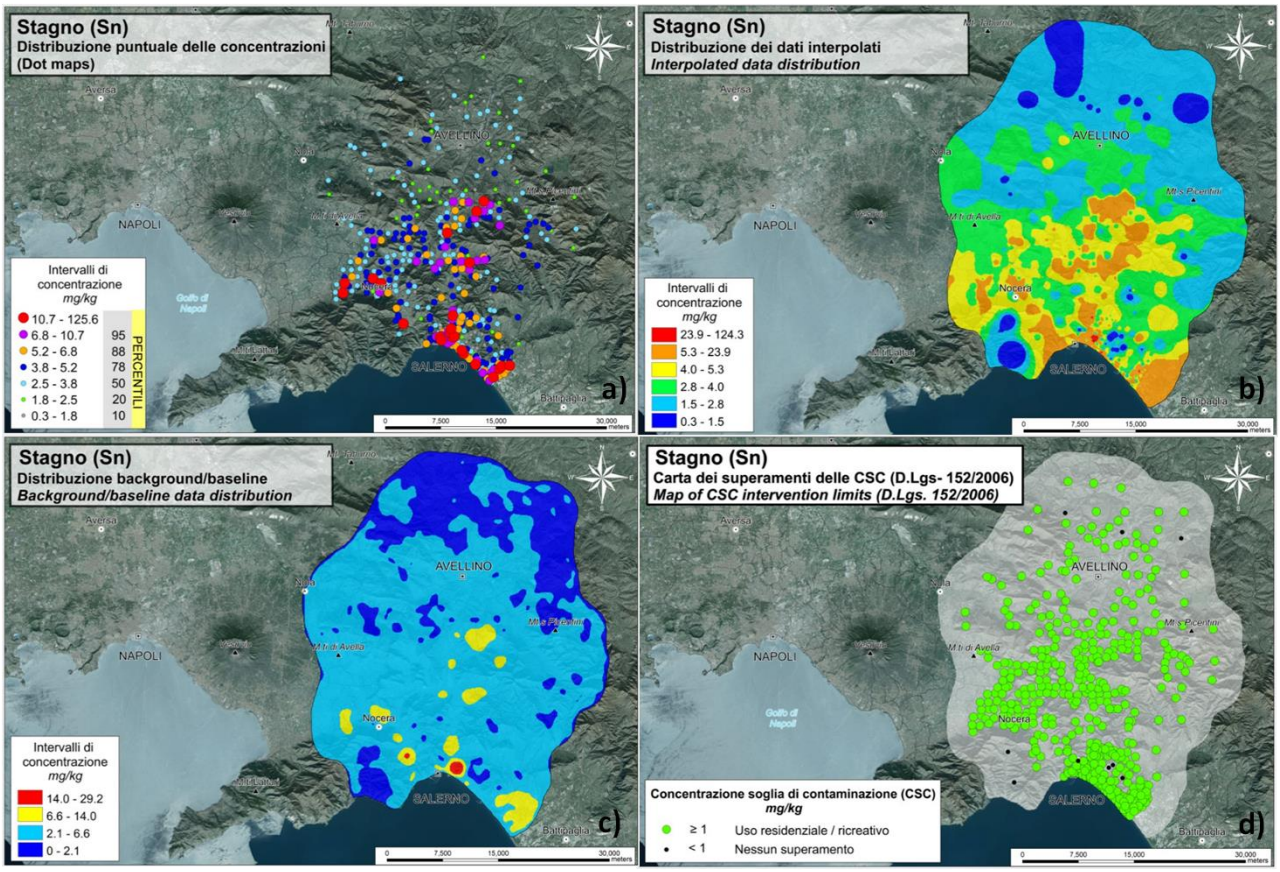


Fig. 3.24:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Sn.*

3.4.1.9 Thallium (Tl)

Thallium concentrations in the analyzed samples varies from 0.13 and 3.05 mg/kg, a lot below the maximum value for Campania region (69 mg/kg),but with a median value a little higher (1.74 and 1.33 mg/kg respectively).

From the dot distribution map is it possible to observe that most of the sampled sites (90%) have low Tl values <1.9 mg/kg. The 5% of the samples have intermediate values, between 1.9 and 2.5 mg/kg, mostly located in Avellino and in the central area. Higher values, >2.5 mg/kg, interest the 5% of the samples, and are grouped in the Solofrana basin, expecially around Mercato San Severino.

The interpolated map shows that the lowest values (<1.55 mg/kg) are located in the northern and southern parts of the area (Sele plain, Salerno, Lattari Mountains, and the areas characterized by silico-clastic lithologies). Thallium concentrations >1.92 mg/kg, and locally >2.30 mg/kg, are located in the Sabato river and Picentini Mountains, in Partenio Mountains and in the western part of Avellino, Celzi, Piano and Mercato San Severino municipalities, and the eastern Sarno plain, areas probably more influenced by volcanic soils, but where cannot be excluded an anthropic impact.

The *background/baseline* map emphasizes that the lower values, <1.7 mg/kg, are characteristic of the silico-clastic deposits in the northern and southern areas. In the

remaining area is better evidenced how high is the influence of the volcanic soils, being the background values in line with those proposed by Cicchella et al. (2005) for vesuvian (2.7 mg/kg) and phlegrean (1.7 mg/kg) areas.

The samples overcoming the CSC threshold value for residential/public use (1 mg/kg) are located in almost all the area, interesting the 81% of the analyzed samples. The Tl threshold values should be renewed, basing on the knowledge of the natural background values, but in this case an attention to the anthropic activities standing in the area, should exists. There are no overcoming of the CSC for industrial/commercial use (10 mg/kg).

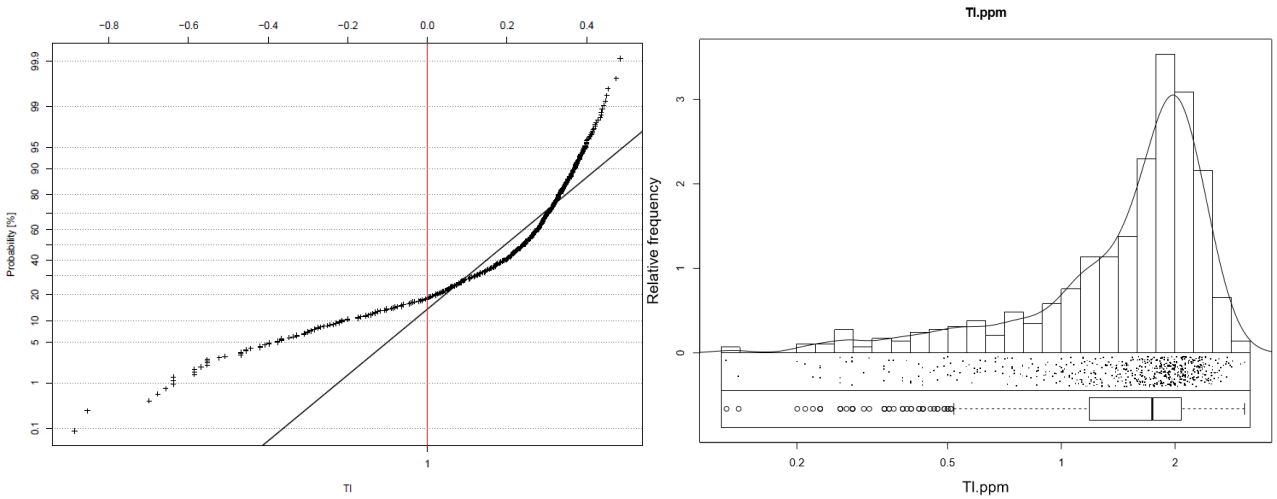


Fig. 3.25:*CP (on the left) and EDA (on the right) plots for Tl in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

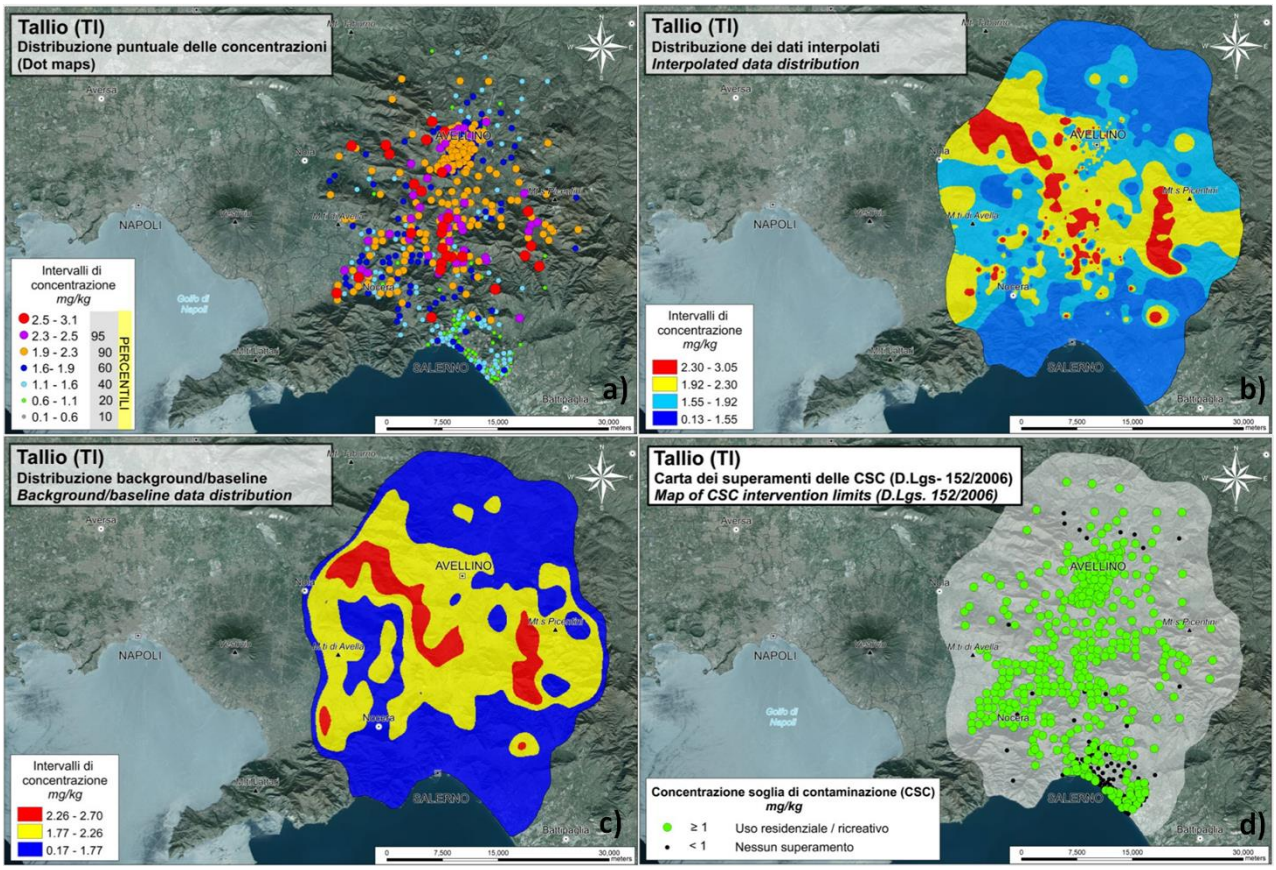


Fig. 3.26:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Tl.*

3.4.1.10 Vanadium (V)

Vanadium concentrations in Campania top soils vary between 14 and 138 mg/kg, quite lower than the Campanian top soils V contents (maximum value 224 mg/kg), but with a higher median value (82 and 60 mg/kg respectively).

The dot distribution map shows that most of the Campania top soils have low V concentrations. Only 5% of the analyzed samples have V contents >109 mg/kg, and are grouped in the Solofrana river valley. Only 2.5% of the sites have concentrations >123 mg/kg, and are concentrated in the south of Avellino.

From the interpolated map is it possible to identify three distribution *patterns* for V concentrations; the first one with low values (<73 mg/kg) in the northern and southern sectors of the area, and in Cilento area; the second one with intermediate values (73-93 mg/kg) in the central zone; the high values (>93 mg/kg and locally >111 mg/kg) are localized in Avellino and south of Avellino, Sarno plain, Piano and Mercato San Severino (Solofrana basin), Sabato river, and Avella Mountains.

The *background/baseline* map shows a trend between 68 and 93 mg/kg. Lower V concentrations (<68 mg/kg) can be found in the northern part of the area, in the Lattari Mountains, and Sele plain. High values (93-119 mg/kg, in line with the natural *background* value of 120 mg/kg established by Cicchella et al., 2005) can be found in some eastern areas

(Sarno plain, Avella Mountains, and Cava de' Tirreni), associated to volcanic lithologies. The same values are found in Solofrana basin, and Picentini Mountains, where, at contrary, cannot be identified geolithologic influences.

The 34% of the samples exceeds the CSC threshold values for residential/public use (90 mg/kg), while there are not overcoming of the CSC for industrial/commercial use. Those samples are located in wide areas in Avellino, Picentini and Avella Mountains, Solofra basin and Sarno plain. The geo-lithologic contribute is evident, but anthropic contribute probably influences the V concentrations >90 mg/kg especially in Solofra basin, in the Sabato river and in the south of Avellino, where the agricultural activities are well developed.

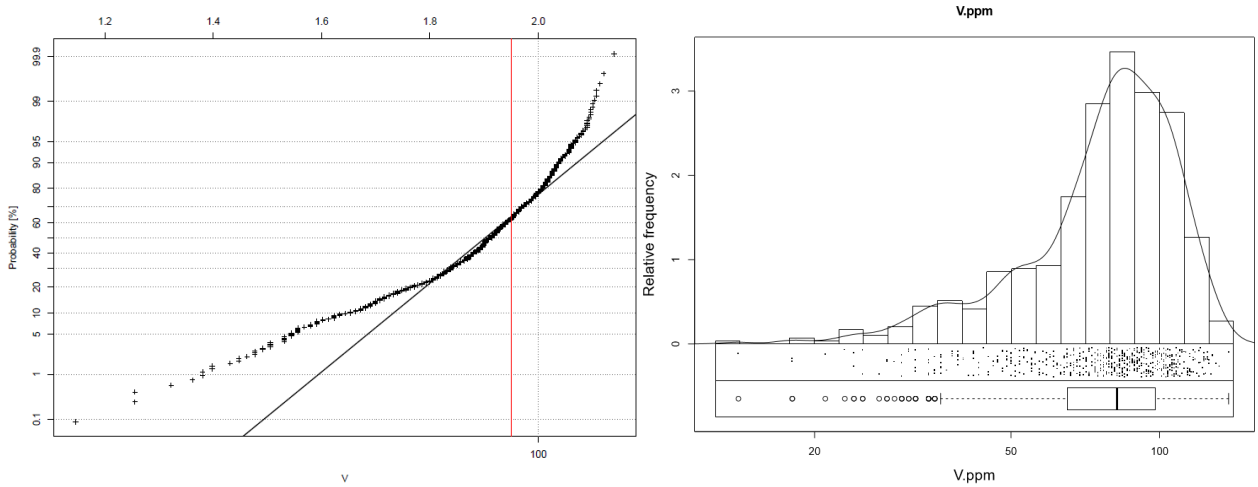


Fig. 3.27:*CP (on the left) and EDA (on the right) plots for V in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

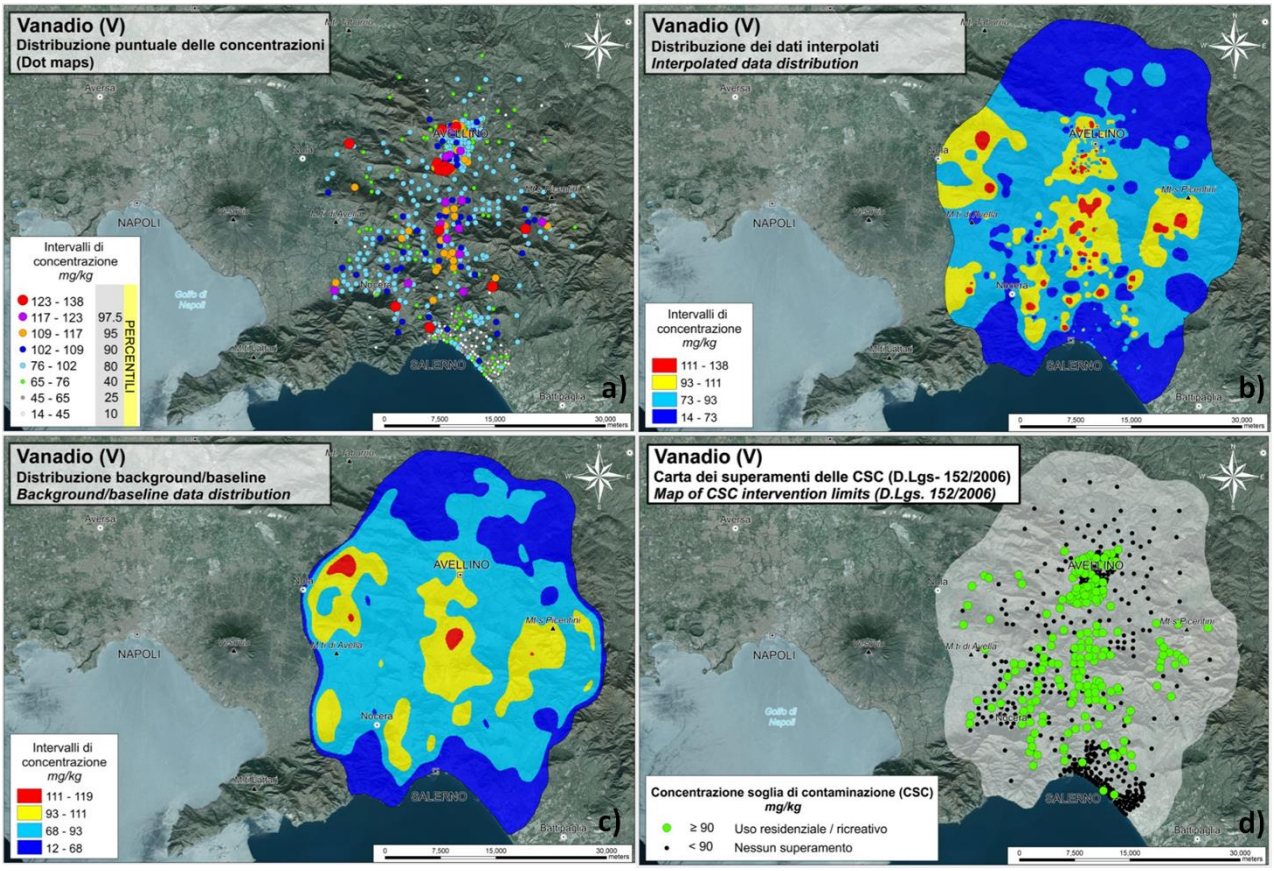


Fig. 3.28:*a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for V.*

3.4.1.11 Zinc (Zn)

The zinc contents in the top soils of the analyzed area varies between 17.9 and 1682 mg/kg, much below the maximum Campanian values (3210 mg/kg), but with a similar median value (101 and 91 mg/kg respectively).

The dot map shows that 2% of the sampled sites have high concentrations of Zn (>504 mg/kg) and are grouped in Salerno and Sele plain. The 6.5% of the samples have Zn contents >261 mg/kg, and are located again in Salerno and, moreover, in Solofrana river valley (Mercato San Severino). The lowest values (<86 mg/kg) are concentrated in the more peripheral and isolated areas.

The interpolated map confirms that the lowest values (<67 mg/kg) are located in small mountainous areas (Lattari, Picentini, Avella, Partenio Mountains). The majority of the territory shows intermediate values, between 67 and 165 mg/kg. Zinc concentrations >165 are located in Salerno (up to the Amalfi coastline), Sele plain, Nocera, and Solofra basin (from Piano to Solofra, Mercato San Severino, Calvanico and Gaiano). Only two small areas in Piano, Salerno and Sele plain have Zn contents between 671 and 1659 mg/kg.

Most of the area has intermediate background values, between 76 and 166 mg/kg. The mountainous areas have low Zn background values (<76 mg/kg). Higher values, between

166 and 464 mg/kg, are clearly related to the areas with major vehicular traffic: Salerno, Amalfi coastline, Solofra basin, and small areas in Sarno plain.

In the maps of the CSC intervention limits, 24% of the samples are above the intervention limit of 150 mg/kg for residential/recreational use, located in Salerno, Avellino and Solofrana basin. Only one sample in Salerno is above 1500 mg/kg, the intervention limit for industrial/commercial use.

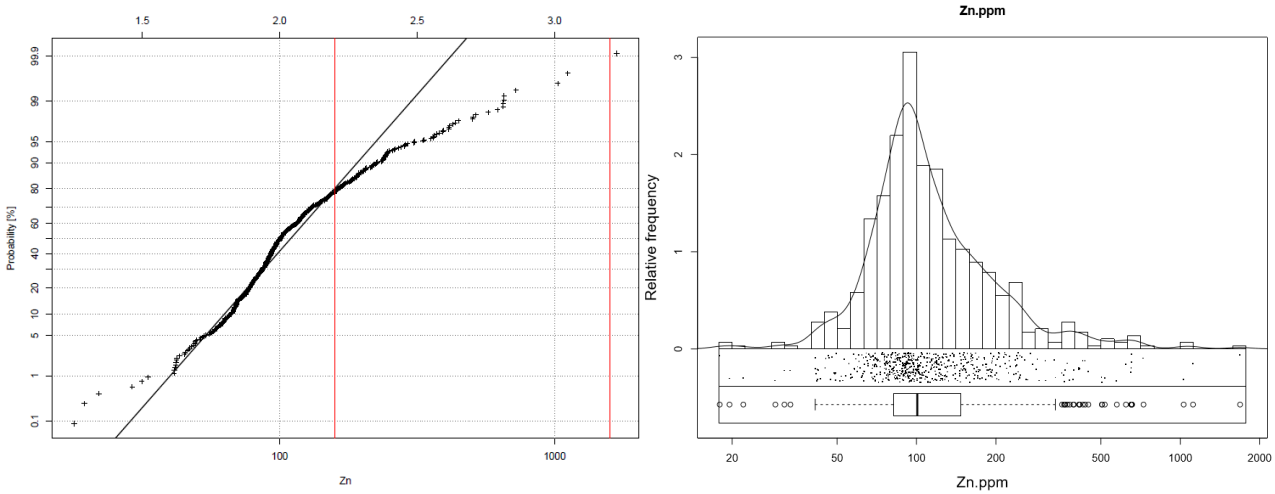


Fig. 3.29*:CP (on the left) and EDA (on the right) plots for Zn in log scale. In the CP plot, the black line represents a straight line forcing the data points; the vertical red line represents the CSC threshold limits established by the Italian Legislative Decree D.Lgs. 152/06.*

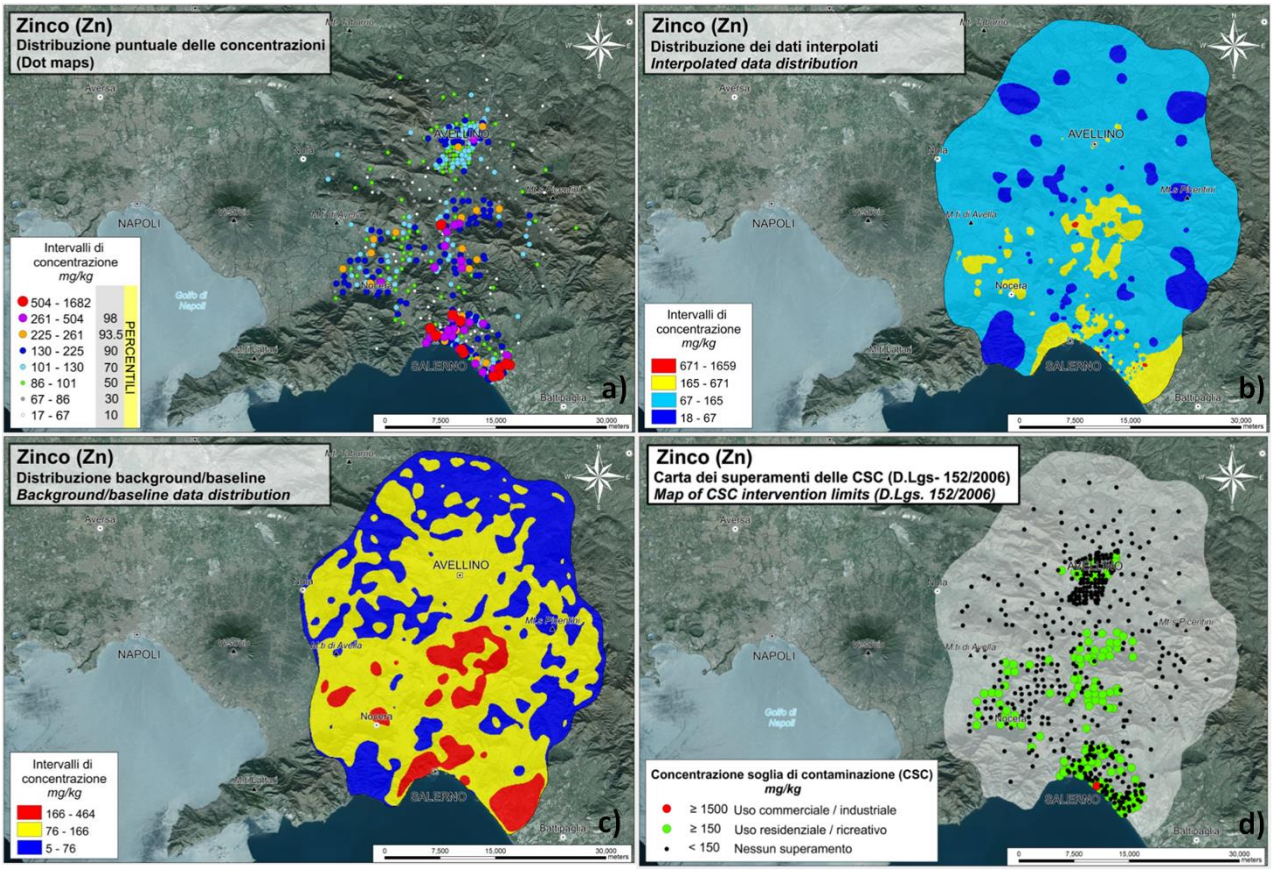


Fig. 3.30*: a) Dot distribution map; b) Interpolated map; c) Background/baseline map; d) Maps of the CSC intervention limits overcoming for Zn.*

3.4.2 Description of the potentially toxic elements with values below the CSC threshold limits

For those elements, the cartographic elaboration is present on the attached dvd.

3.4.2.1 Cobalt (Co)

Co content in the analyzed soils varies from 1.4 mg/kg to 22.8 mg/kg, quite lower than the Campanian maximum value (79 mg/kg), but with a similar median value (11.3mg/kg and 10.2 mg/kg respectively).

From the dot maps is it possible to observe that 90% of the sites have Co concentrations <14.9 mg/kg, and only 2.5% of the samples have Co concentrations >17 mg/kg. Those higher spots are grouped in Avellino area, and some sparse value appear also in Solofra and Sabato River valleys, and in the area north to Salerno and Cava de' Tirreni.

The majority of the territory in the interpolated map shows values <14 mg/kg, compatible with the Campanian interpolated map. The lower values <9.6 mg/kg can be found in the coastal areas (Salerno and Lattari Mountains), and in the north-western part. The values >14 mg/kg are located especially in Avellino city, and in the south of Avellino, where are sited the higher values as well (17.2-22.8 mg/kg), and in Solofrana basin. The higher values can be found also in an area between Nocera Superiore and Cava de' Tirreni municipalities (the eastern slopes of the Lattari Mountains), and in the Sabato river valley.

The *background/baseline* values are in almost all the area in line with the natural *background* values of 3-14 mg/kg, evaluated by Cicchella e al. (2005). Some wide areas show higher Co contents, but compatible with the *background/baseline* values evaluated in the Campania Atlas (< 16 mg/kg).

The CSC map shows that none of the sampled site overcomes the threshold values for industrial/commercial sites, and only one site overcomes the threshold for public/residential use (20 mg/kg).

3.4.2.2 Mercury (Hg)

The Hg concentrations in the analyzed top soil samples are between 3 mg/kg and 922 mg/kg, much below the Campanian concentrations, that have a maximum value of 6775 µg/kg, but with the same median value of 58 µg/kg.

From the dot distribution map is it possible to observe that only 2.5% (97.5° percentile) of the analyzed samples has concentrations >304 µg/kg (the range considered normal by Kabata-Pendias, 2001, is <400 µg/kg). Those samples are concentrated in Avellino and Salerno cities; some sparse sites can be found in the central area. The remaining samples have quite low Hg concentrations.

In the interpolated map is evidenced how the majority of the area has low Hg contents (<150 µg/kg), and especially the northern part has concentrations <30 µg/kg. The higher Hg concentrations can be found exclusively in some small urban areas: Avellino, Salerno, Piano and Solofra municipalities, Siano and the W of Mercato San Severino, Nocera, Cava de' Tirreni, and finally in the Sabato river valley, and in the eastern area of Avella Mountains.

The CSC map shows no overcoming of the CSC threshold values for residential/public use (1000 µg/kg) and for industrial/commercial use (5000 µg/kg).

3.4.2.3 Nickel (Ni)

The Ni concentrations in the analyzed top soil samples vary between 3.8 mg/kg 0.5 and 73.6 mg/kg, below the maximum value for Campanian top soils (101 mg/kg), but with a similar median value (15.3 and 14.7 mg/kg respectively).

The dot distribution map shows that only 3% of the sampled sites (97° percentile) have Ni concentration >29.8 mg/kg and 95% of the sites (95° percentile) is below 21.6 mg/kg. The higher values are located in the northern part of the study area, in Salerno and Sele plain, and in the Sabato river.

The interpolated map shows how the majority of the territory has low Ni contents <19 mg/kg, probably influenced by the volcanic soils. Nickel tends to be absorbed by clay minerals and Fe-Mn hydroxides, and this is evidenced by the Ni content that varies between 19 and 41 mg/kg in the northern and eastern parts of the study area, where is clearly influenced by clay and floodplain deposits. The highest Ni values, >41, cannot exclude an anthropic contribute, being concentrated in the Sabato river, and in a wide area to the north-west of Avellino, interested by an intense agricultural activity.

The *background/baseline* map shows Ni concentrations in a range between 14-20 mg/kg in most of the territory. Background values between 20 and 42 mg/kg can be observed in the northern and eastern areas, characterized by clayey deposits. The highest background values (>42 mg/kg) can be observed only in a small area in the north-west of Avellino city.

No overcomings of the Ni CSC threshold values for residential/public use (120 mg/kg) and industrial/commercial use (500 mg/kg) can be observed.

3.4.2.4 Selenium (Se)

Selenium concentrations vary between 0.05 and 1.5 mg/kg, with a median value of 0.5 mg/kg, values similar to the Campanian top soils (maximum value 2.4 mg/kg and median 0.4 mg/kg).

The dot distribution map shows 2.5% of the samples with Se concentrations >1 mg/kg. High values, >0.8 mg/kg, are grouped in Avellino, south of Avellino, and Nocera. Intermediate values (0.6-0.8 mg/kg, 20% of the samples) can be found in the main urban areas (Avellino area, Solofra, Mercato San Severino, Sele plain, Salerno).

The *background/baseline* map shows that the lowest Se concentrations, <0.37 mg/kg, can be found in the northern area and on the Lattari Mountains. The central area, and Salerno and Sele plain are characterized by intermediate values (0.37-0.58 mg/kg). Also the highest values, between 0.58 and 1.38 mg/kg, in Avellino, Picentini Mountains, and Sarno plain, are compatible with the natural background values evaluated by Cicchella et al. (2005) (0.2 - 1.1 mg/kg). Only a small area on the Sabato river has Se background values >1.38 mg/kg.

Selenium concentrations are always lower than the CSC threshold values established by the D.Lgs 152/06 for residential/public use (3 mg/kg) and industrial/commercial use (15 mg/kg).

3.5 Risk analysis

The same risk analysis GIS based methodology, exposed in the previous chapter, has been used in this detailed area. The major detail will give the possibility to select one or more restricted areas where a follow up activity must be carried out. Those gradual steps are a useful and low cost instrument for the administrations, that, as a consequence, are able to take decisions for guaranteeing the safety of the population. Only in those areas where the follow up activity gives negative results, reclamation can be carried out.

Although the GIS data, needed for the risk analysis, should be intensified, due to the higher resolution, we carried out the assessment with the same regional data, for a question of time. The results were however satisfactory, and are shortly exposed in the following paragraphs.

3.5.1 Potential hazard

The potential hazard map (Fig. 3.31) exposes that the lowest potential hazard is only in some mountainous, isolated areas. Most of the area has the contemporary presence of 1-4 potentially toxic elements, in particular Sn, Tl and Be. All those elements have CSC threshold values that should be renewed, because they do not take into account the natural background of the area. To support this principle, in the Environmental Geochemical Atlas of Campania Region, we proposed the delimitation of 10 different areas with specific geolithologic characteristics, for which we defined the minimum and maximum *background/baseline* values of the potentially toxic elements. It will be task of the Administrations to integrate these data in the environmental law.

Wide areas with intermediate potential hazard see the contemporary presence of 5-6 potentially toxic elements. These are in particular from S to N:

- An industrial area at the western margin of Sele plain;

- An area between Vietri sul mare and Cava de' Tirreni, that is probably interested by illegal spills.
- Wide areas of Solofrana river valley: from the Sarno plain and municpality, to Nocera Inferiore, Superiore, Roccapiemonte, Castel San Giorgio; Baronissi, Fisciano, Gaiano, Piano, Solofra, where 160 tanning plants are sited;
- A wide area on the Picentini Mountain and Sabato river;
- The area around Avellino: Aiello del Sabato, Atripalda, Grottolella, where the agricultural and industrial activities are highly diffused.

The highest risk is for the areas that are subject to the contemporary presence of 7-8 potentially toxic elements (As, Cr, Cu, Pb, Sn, V, Tl, Zn):

- Two small areas dedicated to public parks, one in Salerno and one in Nocera Inferiore;
- The southern part of Mercato San Severino, up to Oscato and Spiano municipalities;
- Carifi, and a wide area between Ciorani and Bracigliano municipalities;
- An area to the w of Piano municipality;
- An area on the south-western Picentini Mountains;
- An agricultural area in the north of Solofra municipality;
- Two agricultural areas in the north and in the south of Avellino.

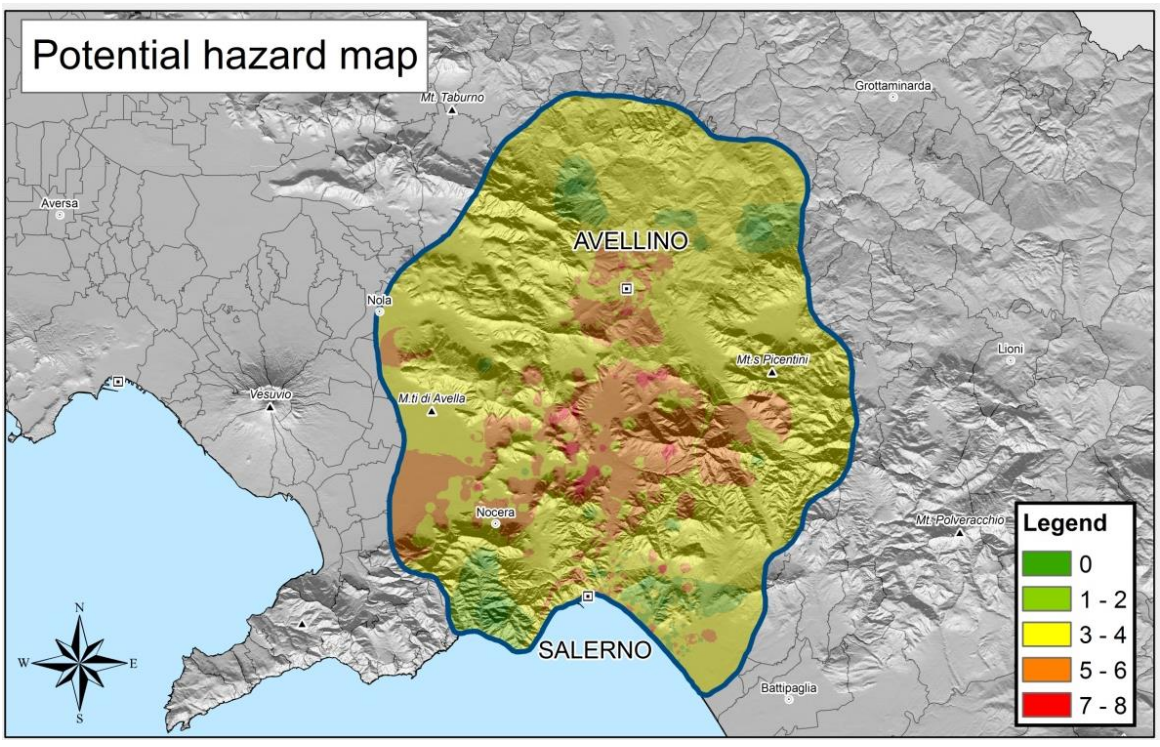


Fig. 3.31: *Potential hazard map for the selected area. In this case as well there is the contemporary presence in the same area up to eight different potential hazardous elements.*

3.5.2 Human health risk

The main contribute for the human health risk in the area comes from the direct contact with the soil, and the groundwater exposure routes, both reaching scores up to 100 (Fig. 3.32a-d). Especially the direct contact with the soil shows wide areas with highest risk (54-100), probably due to the presence on the territory of extended agricultural and residential areas. Secondary exposure routes, with scores reaching 76 and 66 respectively, are contamination of surface and diffusion in air.

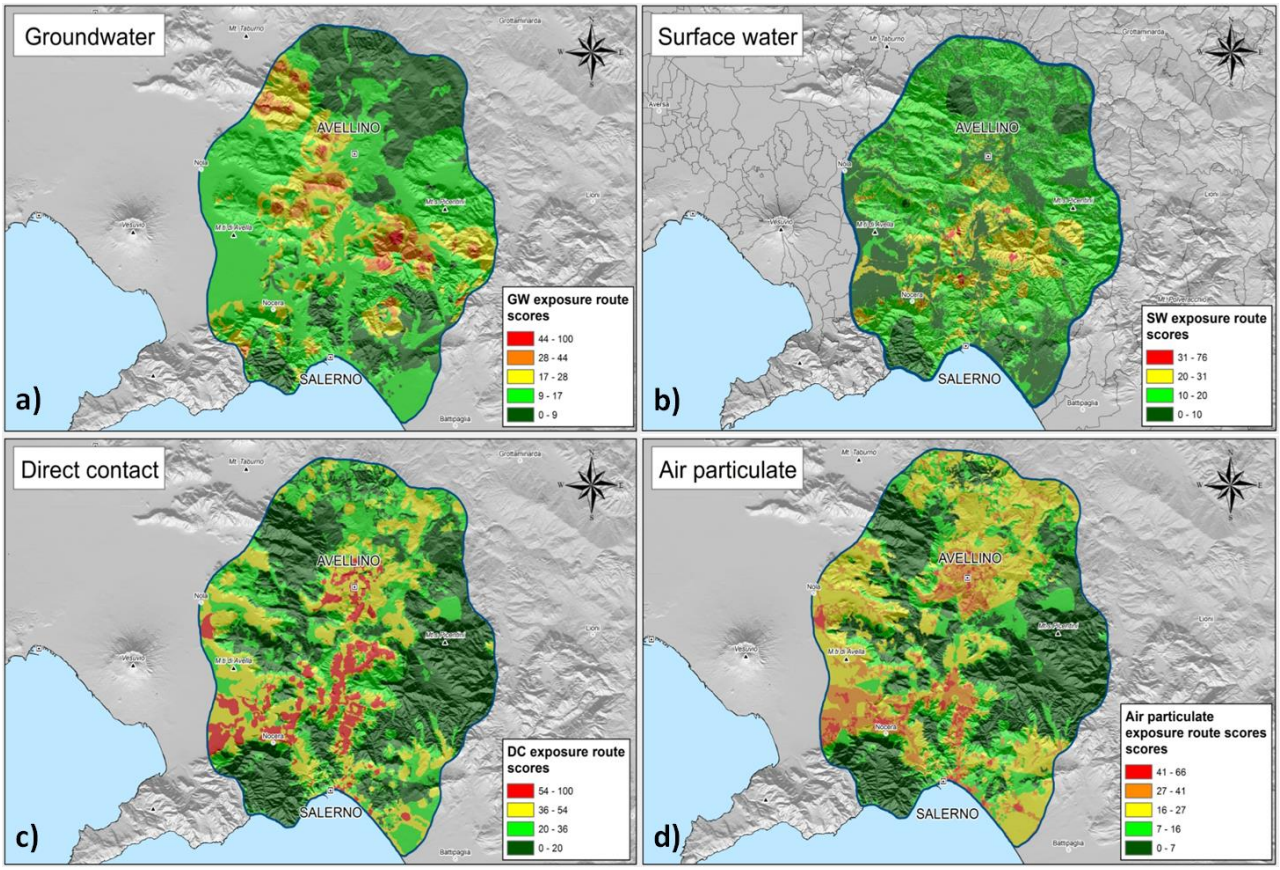


Fig. 3.32*: a) Groundwater exposure route map; b) Surface water exposure route map; c) Direct contact exposure route map; d) Air particulate exposure route map.*

In the overall risk map (Fig. 3.33), most of the mountainous and isolated areas have the lowest scores, less than 20. The land use is a parameter that affect a lot the scores distribution. The agricultural areas are those with scores higher than 20, and most of the urban areas shows scores higher than 40.

The areas where the follow up activity should be carried out are those with scores higher than 60, classified with high risk. Those are in particular:

- An area in Salerno city, dedicated to public park;
- An area in Nocera Inferiore, really close to another public park;
- A small agricultural area in the south of Avellino city;

- An area in Spiano and Oscato municipalities;
- Two urban areas respectively in the W (Carifi municipality) and E of Mercato San Severino municipality.

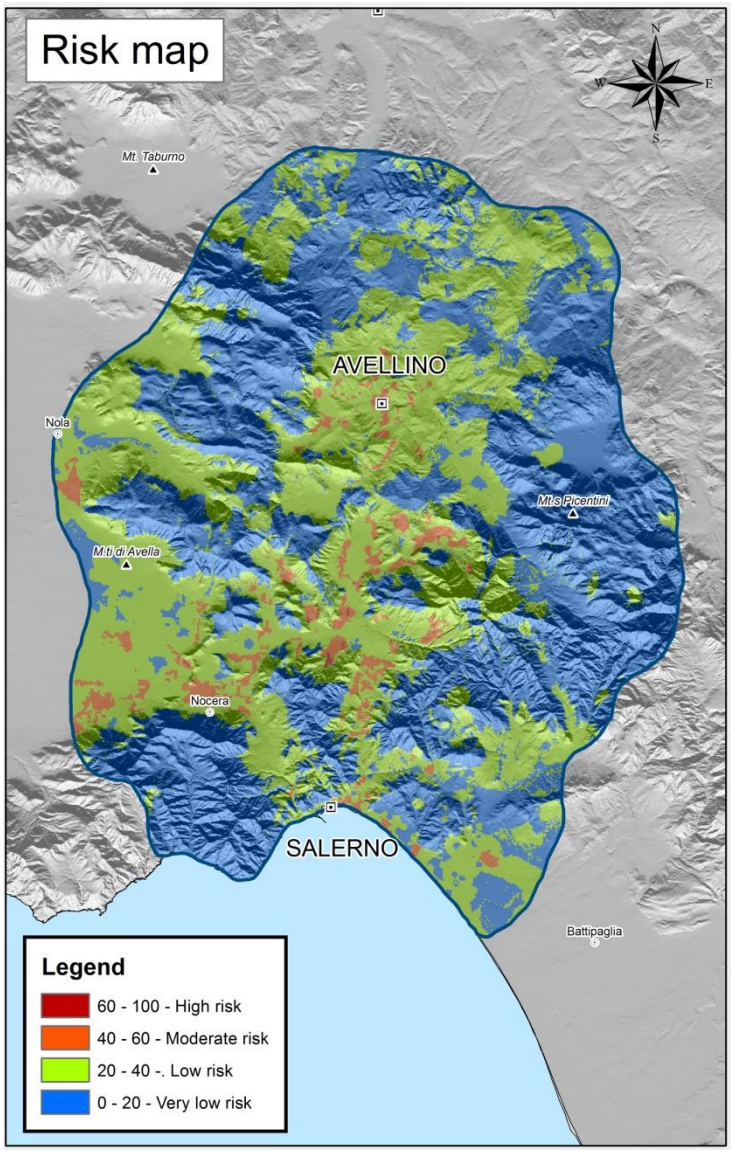


Fig. 3.33*: Overall risk map for the selected area.*

In these areas where the risk for the human health is high, is important that the administrations use their efforts to guarantee the safety of the population. Follow up activities must be carried out in order to know if remediation actions are needed.

Conclusions

A multiscalar environmental risk assessment on the top soils of Campania region has been proposed in this thesis. The developed methodology provides a new approach for assessing the risk for human health in intensive and extensive contaminated regions. A European-wide accepted methodology for the preliminary assessment of human health risks at single contaminated sites (PRA.MS) was the base for this study. In order to adapt this methodology to the regional level, GIS software tools were used in order to evaluate effectively the spatial distribution of different parameters. The methodology consists of a multi-element characterization of the soil in a regional territory, where all possible exposure routes for contamination are evaluated.

The regional approach is a valid tool for the administrations' decision-making process to select the potentially hazardous areas, and to use cost-effectively the available resources. A fundamental step in guaranteeing the protection of soil, and consequently the health of the population, is focusing the monitoring and action systems on selected potentially hazardous areas, so that the monitoring efficiency is increased and the costs are minimized. Every kind of decision-making process with respect to land use and population health would be simplified through the elaboration of a regional risk distribution map. The developed risk assessment methodology should be applied in each risky area, characterized by diffuse contamination, where the prioritization of the potentially hazardous areas would be otherwise difficult.

Another possible advantage of having a regional mapping of environmental risk is the application in epidemiological studies, already carried out by Albanese et al. (2013). They found that there is a good spatial correlation between the incidence of some cancer types and the distribution patterns of contaminants in stream sediment. The use of the regional risk map would be more appropriate than the single element distribution maps, as it provides a more complete views of the environmental and sanitary risk.

After selecting the potentially hazardous areas it was possible to apply the same methodology in a more restricted area, following an improvement of the geochemical database with a high density sampling. This was useful in order to select the areas where a follow up risk assessment must be carried out. Some of these are of particular significance, being located in public parks or in agricultural areas. The in situ measurements can confirm if remediation actions are needed to guaranteeing the safety of the population.

The proposed method can still be improved by the quantification of uncertainty and by the collection of more detailed and accurate data and information, both at regional and reduced scale, so that the accuracy of the risk assessment will still be better.

Chapter 4 – Other activities: Humus samples as an indicator of long-term anthropogenic input – a case study from southern Finland

Minolfi, G., Jarva, J., Tarvainen, T., 2017. *Humus samples as an indicator of long-term anthropogenic input – a case study from southern Finland*. J. Geochem. Explor, in press.

Abstract

Humus has been recognized as one of the best sampling media for mapping regional environmental contamination. However, because of the complex and not completely understood humus geochemistry, reflecting in different amounts the underlying geology, the biosphere's activity, and the airborne deposition, its application is still not widespread.

This study was conducted within the framework of a comparison between regional humus and topsoil geochemical baseline data, in order to analyze the element concentrations in humus and to find possible similarities to the underlying geology and long-term atmospheric deposition. The analyzed samples formed part of a geochemical mapping program carried out by the Geological Survey of Finland (GTK) from 2002, and the humus samples collected over an area of 37,000 km2 in southwestern Finland are elaborated here for the first time. Altogether, 816 sample pairs (humus and topsoil samples) were selected for statistical analysis and a correlation analysis between the element concentrations in humus and minerogenic topsoil and between the element content vs. the content of organic carbon.

Statistical graphs constructed for 31 elements revealed that most of the elements have a completely different distribution of concentrations in humus and topsoil samples. The concentrations of some elements in humus, such as K, Mg, Fe and Al, are controlled by the content of mineral matter, derived from soil dust (<0.002 mm). Other elements, such as As, Bi, Cd, Co, Cu, Mo, Ni, Pb, Rb, Th, V and Zn, showed evident outliers in humus samples, with a probable anthropogenic origin. In order to explain these anomalous high values in humus, the geographic distributions of these elements in humus and topsoil were analyzed and then compared with deposition data obtained from a national moss surveys.

According to the results presented here, the humus element concentrations are more strongly affected by atmospheric inputs than by the lithogenic contribution, which is opposite to the case for the topsoil samples. The topsoil element distribution maps clearly show the strong relationship with the bedrock geology (such as the relationship of the Ni distribution with the Ni-Co-Cu metallogenic area of the Tampere Region); the humus concentration distributions show a strong correlation with the anthropogenic impact of known deposition from local pollution sources. No long-range transport was clearly identified, but point sources, such the Pori-Harjavalta smelters, and more densely populated and industrialized areas, such the city of Tampere and the coastline from Porvoo to the capital region of Helsinki, cause locally high anomalies in humus concentrations, even

many years after the decreasing of industrial inputs. Additional humus samples with a sufficient sampling density close to city centers and industrialized areas should be collected in order to improve knowledge of element concentrations in humus and anthropogenic inputs to the topmost layer of ground surface, as well as potential risks to the environment and human health.

4.1 Introduction

In the cool temperate areas of the world, in regions such as Fennoscandia, Russia, and Canada, the climate gives birth, in the first millimeters to centimeters of the soil, to an organic rich layer consisting of dead plant material. This humus layer has often been regarded as one of the best sampling media for mapping regional environmental contamination. This is because of the strong geochemical contrast between anomalous and background concentrations resulting from its capacity to accumulate high levels of trace metals (Steinnes, 1984; Niskavaara et al., 1996, Henderson et al., 1997). However, its application is still not widespread, because humus has a very complex geochemistry, reflecting the interplay between the atmosphere, biosphere, and lithosphere.

A common belief is that the composition of surface soil horizons depends on the soil parent material and thus on the underlying geology. The parent rock from which the soil develops has an influence on the chemical composition of the newly formed soil (Reimann et al., 2014), and, consequently, the composition of the soil horizons, can have a strong impact on the geochemistry of humus (Lax et al., 1995). In Finland, the most common soil parent material is not locally weathered regolith but glacial till. Other typical soil parent materials are fluvial sorted sediments and fine-grained lacustrine or marine sediments. Glacial till that has been transported relatively short distance by the ice sheet reflects better the composition of underlying bedrock than other soil parent materials in Finland. Some elements can be enriched in the humus layer without any airborne deposition. Rankama and Sahama (1950) reported that Ag, Au, Be, Zn, Cd, Sc, Tl, Ge, Sn, Pb, As, Mn, Co, and Ni are enriched in the humus layer by simple physical processes such as evaporation and filtration recurring year after year (the so-called Goldschmidt enrichment principle) (Goldschmidt, 1937). Rare elements will often be preferentially dissolved and concentrated in the small amount of water circulating through decaying organic matter. These solutions enter plants and a major part of the dissolved salts are deposited in leaves and other parts due to high evaporation. Some elements are more easily leached from yellow withering leaves, while sparingly soluble or insoluble constituents of other metals, such as hydroxides and protein and humic complexes, are retained in the humus layer. This is why the organic and topsoil horizons are found to be geochemically distinct entities (Reimann et al., 2015a). Pollutants in the humus layer can derive from natural or anthropogenic sources (Lax et al., 1995), but in each case, the elements adsorbed by humus are retained by it for at least the lifetime of

the forest (Suchara and Sucharova, 2003), so that the presence of pollutants in humus reflects long-term accumulation (Reimann et al., 1998, Kinnunen et al., 2003).

Following an initial survey in 1977 (Allen and Steinnes, 1980), it was immediately clear that metal concentrations in the humus layer are not necessarily associated with the geochemistry of the underlying mineral material (Steinnes and Njåstad, 1995). Sampling of the humus layer, together with moss, used in the biomonitoring of the atmospheric deposition of heavy metals, was carried out in a large-scale survey in Norway in 1977 (Rambæk et al. 1980), and in another national sampling in 1985 (Bølviken et al. 1987), to understand the different mechanisms supplying metals to the organic surface soil horizon (Steinnes and Njåstad, 1995).Other investigations in several regions were also carried out in these years (Siccama et al. 1978, Heinrichs et al. 1980). Four different sources of metals inthe organic surface layer were identified: bioturbation, the "vascular pump", atmospheric input of marine origin, and airborne pollution (Steinnes and Njåstad, 1995). From this time on, in all of the European surveys on atmospheric deposition based on moss analysis (Rühling, 1992, 1994; Rühling and Steinnes, 1998), participants were asked to sample and analyze humic surface soil samples in addition to moss samples (Nygård et al.,2011).

In Norway, the organic-rich surface soil horizons were also found to be affected by atmospheric inputs from natural and anthropogenic sources: long-range atmospheric transport of pollutants is the dominant source of Cd, Sb, Pb, and Bi, while local point sources of pollution provide significant contributions to soil concentrations of Ni, Cu, Zn, As, Mo, and Cd (Nygård et al., 2011).In the Czech Republic, most anomalies visible in distribution maps can be linked to known industrial sites, mining, power plants, or urbanization, and humus was therefore concluded to be a suitable sample material to depict the contamination history at the national scale (Sucharova et al. 2011). In a small town in western Finland, Peltola et al. (2003) analyzed the concentrations and distributions of 36 chemical elements in glacial till and humus samples taken from urban and rural areas as well as man-made, urban soil samples. The majority of the elements occurred in higher concentrations in the urban than the rural humus samples. Statistical and spatial interpretations of the humus data revealed that traffic (Pb, V and Ni), metal industry (Pb, Zn, Bi, Sb and Cr), an abandoned shooting range (Pb and Sb) and other anthropogenic sources contribute to higher metal levels in the urban humus. On the other hand, Tamminen et al. (2004) compared the concentrations of 15 elements in the humus layer of coniferous forests with the corresponding data for moss samples in Finland, concluding that for most elements, concentrations in the humus layer were a poor indicator of current atmospheric deposition levels, at least in a relatively unpolluted region such as rural areas in Finland. In another low density sampling carried out in Fennoscandia (Lax et al., 1995), comparing humus with glacial till and moss samples, geological features were found to exert only a weak influence on the regional distribution of elements in humus (only carbonate rocks were easy to detect from Ca and Sr contents).Pollution was the source of high concentrations of Pb, Cd, and Zn in southern Sweden and southern Norway, and the authors concluded that the humus horizon could be suitable for environmental monitoring if

included in global geochemical mapping, at least in temperate, glaciated areas. In an area in Canada (Henderson et al.,1998), the trace element geochemistry of humus and till was evaluated to reflect smelter contamination in the environment. Total concentrations of all smelter-related elements in humus decreased as a function of distance from the smelter, independently of the total organic carbon content, and exceeding the concentrations in till. The smelter-derived particulates were confirmed by SEM examination. Other studies were carried out on humus samples using microbeam analysis. The smelter-derived dust were probably the primary mechanism for delivery of metals to humus, but the particles were not the current primary residence site of metals in the humus. This suggested that, soon after deposition, weathering processes have released metals and other elements from the dust to the humus (Knight and Henderson2006).

Later, Reimann et al. (2009, 2015b) concluded that enrichment of potential toxic elements in forest soil O-horizons in Norway is often caused by natural processes and has little or no connection with anthropogenic sources. The anthropogenic impact is often very local, and in their survey with a low sample density, Reimann et al.(2015b) did not observe such an impact, as samples were not taken close enough to a city or industrial areas.

This study was carried out In the framework of a comparison between regional humus and topsoil geochemical baseline data, in order to analyze the element concentrations in humus and to find possible similarities with underlying geology and long-range atmospheric deposition. Humus sampling was for the first time carried out with short spacing and centered on an area in southern Finland with known local sources of pollution and urbanization that have led to the atmospheric deposition of heavy metals. The analyzed samples were part of a geochemical mapping program that provided the first estimates of baseline concentrations of inorganic substances that are also anthropogenic contaminants on a national level. The Geological Survey of Finland (GTK) carried out nationwide geochemical mapping of glacial till in Finland on a reconnaissance scale in 1983 (Koljonen, 1992) and on a regional scale during the period from 1984 to 1992 (Salminen, 1995). These surveys provided information on the natural elemental distribution in subsurface sediments (subsoils), mainly glacial till. However, some important trace elements such as As, Cd, and Pb were missing from the determinations, and subsoil samples do not reflect the diffuse contamination of the ground surface from anthropogenic sources. Thus, GTK continued geochemical mapping in 2002 by studying geochemical baselines around the city of Porvoo, located in the Uusimaa region of southern Finland, using topsoil (uppermost 25 cm under the humus layer), subsurface sediment, and humus samples (Tarvainen et al., 2003). The sample profiles represented the most common mineral soil parent materials of the region: glacial till, fine-grained sediments, and sand. Subsequently, GTK extended the geochemical baseline sampling of humus, topsoil, and subsoil to larger area in southern Finland (around the cities of Espoo, Hämeenlinna, Tampere and Pori). Humus samples collected in this area are for the first time elaborated in the present work.

4.2 Study area

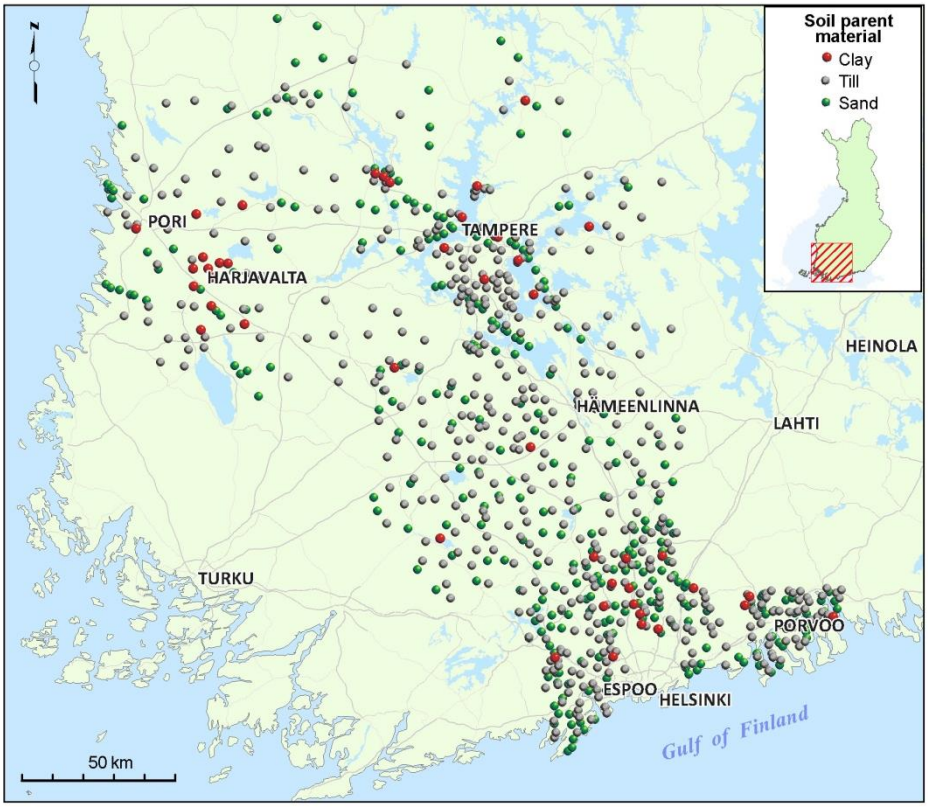


Fig. 4.1*: Sampling sites of humus and topsoil sample pairs including to the geochemical baseline mapping in Southern Finland during 2002 – 2013. The total number of samples pairs is 816.Topographic map © National Land Survey of Finland and ICT Agency HALTIK.*

The geochemical sampling area covers nearly 37,000 km2 of southern and western Finland (Fig.4.1). A large part of the area is forested and samples were taken from areas without any intensive land use. However, several cities and municipalities are located within the area, of which the commuter cities and municipalities of the Helsinki Metropolitan Area (Hyvinkää, Järvenpää, Kerava, Kirkkonummi, Nurmijärvi, Sipoo, Tuusula, and Vihti), the city of Hämeenlinna, the Tampere Region (Tampere, Lempäälä, Nokia, Orivesi, Pirkkala, Kangasala, Vesilahti, and Ylöjärvi), and the city of Pori comprise the most urbanized areas. From the Helsinki Metropolitan Area, only samples from Espoo were included in this study. The population is centralized in urbanized areas with about 370,000 inhabitants within the Tampere Region, about 300,000 within the commuter cities and municipalities of the Helsinki Metropolitan Area, about 270,000 in Espoo, about 140,000 in the city of Pori and its neighboring municipalities, and about 95,000 inhabitants in the city of Hämeenlinna and its neighboring municipalities. The city of Porvoo has about 50,000 inhabitants.

Several industrial activities with a long history have been carried out within the geochemical sampling area presented in this paper. Especially the city of Tampere, but also its neighboring cities and municipalities are known as industrial pioneers in Finland. This area has manifold, long-term industries such as the metal and chemical industries, textile manufacturing, pulp and paper production, and rubber manufacturing. The city of Pori has

also a long industrial history of textile manufacture and the metal industry, which followed the establishment of metal refineries in Pori and Harjavalta. Harjavalta has one of the largest smelters in Finland. Metal and machine manufacture takes place in the city of Hämeenlinna, while in the southernmost part of the study area, in Porvoo, there exists an oil refinery. The study area has one active mine in Kutemajärvi, Orivesi (Au). In addition, four closed mines are located in the study area (Haveri (Au, Cu), Ylöjärvi (Cu, W), Kovero-oja (Ni, Cu), and Kylmäkoski (Ni, Cu).

The whole study area is located in the Paleoproterozoic Svecofennian Domain. The bedrock of the domain is predominantly composed of metasedimentary rocks, metavolcanic rocks, and granitoids. The northern part of the study area belongs to the Central Finland Granitoid Complex. The area between the cities of Tampere and Hämeenlinna can be divided into two main geological subdivisions, the Pirkanmaa and Häme belts. The northern part, the Pirkanmaa belt, is dominated by Svecofennian and Karelian mica schist, mica gneisses, and migmatites. It partly overlaps the nickel, cobalt, and copper-rich Vammala metallogenic area. The southern part, the Häme belt, is dominated by Svecofennian and Karelian mafic to intermediate metavolcanic rocks (Kähkönen 2005). Both areas are enriched in Au, As, Ag, Co, Cu, Li, Mo, P, Sb, U, and Zn (Koljonen 1992, Backman et al. 2006). Jotnian sandstones are found in the area between Pori and Harjavalta in the west. The southernmost part of the study area is dominated by metavolcanic rocks, granitoids, and pegmatites (Geological Survey of Finland 2016a).

The geological history of the study area is connected with the deglaciation history of the Scandinavian ice sheet and different phases of the Baltic Sea Basin during postglacial times. At the end of the last glaciation, the majority of the area was influenced by the different stages of the Baltic Sea and covered with water. Only the most eastern parts of the Tampere Region and the highest points of the Hämeenlinna surroundings were supra-aquatic. The area has gradually emerged from the sea, and continuing land uplift still exposes new areas from the sea in the most western parts of the area. Thus, the age of soil deposits differs greatly within the study area.

Under the ice sheet, a compact layer of basal till was formed, and when the ice margin retreated, the land was covered with loose glacial till. These till layers smoothed the landscape by filling valleys and covering bedrock areas. Thick fine-grained sedimentary deposits cover the moraine and bedrock valleys in sub-aquatic areas. Various landforms related to ice sheet retreat and melting of the ice are found all over the area. The Salpausselkä end moraine and related formations dominate the areas south of the Tampere Region. The southern part is characterized by ice marginal ridges, hummocky moraines, drumlins, and glacio fluvial deposits. On the western coast, organic-rich fine-grained sediments are common (Geological Survey of Finland 2016b). The thickness of overburden sediments is highest on the western coast, while on the southern Finnish coast (the Helsinki

Metropolitan Area), the average thickness is low, and thin overburden and bedrock outcrops are common (Geological Survey of Finland 2015).

The most frequent soil types(WRB classification) in the study area are Haplic Podzols (37%), Stagni-VerticCambisols (20%), Dystric Leptosols (16%) and Eutric/DysticHistosols (10%) (Yli-Halla et al. 2003, Natural Resources Institute Finland 2017).Podzolisation is the principal soil-forming process in the forested soils in Finland (Aaltonen, 1952). Typically, podzol is comprised of O (organic), A (eluvial), B (illuvial, enrichment), and C (parent material) horizons in Finland. It is formed in moraine and other coarse-grained sediments, where water is easily infiltrated into the groundAreno- and leptosols, which are weakly developed soils, are typical in coastal areas with a thin overburden and bedrock areas.

4.3 Materials and methods

Quaternary geological maps (scale 1:20 000) were used to select representative sample sites for the most common mineral soil types in study areas. The sample sites were selected so that single point sources of anthropogenic influence were avoided. Three dominant soil parent materials were selected for sampling: sand, glacial till, and fine-grained sediments. Samples were taken from single pits at pre-selected sites. Topsoil samples were taken from the uppermost 25-cm layer of the mineral soil profile under the humus layer, and subsurface sediment (subsoil) samples were taken from a 25-cm layer of unweathered soil parent material. Topsoil samples were dominated by material from the illuvial B horizon in sand deposits and in soils developed on glacial till. Soils developed on fine-grained sediments were often arable land, and the topsoil sample represented the plough layer. Humus samples were collected around the minerogenic soil sample pits where a humus layer was present; humus samples were not available from agricultural land. Each humus sample was a composite sample from at least five locations around the minerogenic soil-sampling pit. All points were selected at a sufficient distance from the nearest trees to avoid ‘‘throughfall’’ precipitation from the trees. The living surface vegetation, fresh litter and large roots and rock fragments were removed. Altogether, 816 sample pairs (sample sites with both humus and topsoil samples) were collected in southern Finland during 2002–2013 (Fig. 1). The samples were dried at 40 °C in the laboratory and sieved to obtain the <2 mm size fraction. Minerogenic soil samples were analyzed using aqua regia extraction (ISO 11466) and humus samples using concentrated nitric acid leach (US EPA 3051A). Altogether, 37 elements were analyzed by ICP-AES or ICP-MS. Mercury was determined with an Hg analyzer using apyrolytic-based method (AMA 254). In addition to element concentrations, pH was determined and separate carbon measurements were made. Loss on ignition (LOI) values were measured from humus samples (Tarvainen et al., 2009).

All 816 sample pairs (humus and topsoil samples) were selected for statistical analysis. The sampling area extended from the Helsinki Metropolitan Area to the Tampere Region

and the coastline of Pori (Fig. 4.1). The sample pairs were classified according to the topsoil sample parent material: 295 sand deposits, 486 glacial till, and 35 fine-grained sediment (mostly clay) samples.

While major processes, such as plant litter decomposition, nutrient, and water uptake occur in humus layer (Ponge et al. 1998), above ground vegetation and humus layer have close connection. The type of above ground vegetation was not recorded in detail in field observations, but the most common land use category of the study sites was forest. According to photographs taken from the sites, samples were mainly taken from coniferous forest (spruce, pine) of various ages.

The data were combined in a single database in IBM SPSS software for the first statistical analysis. Tables reporting the median, maximum and minimum element concentrations (Table 4.1), and histograms were constructed for all humus and topsoil samples combined, and separately for the different soil parent materials in order to examine whether there were differences in the element distributions. For 35 elements (Ag, Al, As, B, Ba, Be, Bi, C, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, and Zn), a comparison between humus and topsoil was possible, while three elements (Si, Li, Br) were analyzed only from humus samples.

Table. 4.1: *Main statistical parameters for humus and topsoil samples from southern Finland sampled during 2002–2013. Number of sample pairs = 816.*

	Humus			Topsoil		
	Median	Minimum	Maximum	Median	Minimum	Maximum
Ag (mg/kg)	.180	.050	7.10	.060	.005	.910
Al (mg/kg)	2895	664	17100	12200	412	49800
As (mg/kg)	1.89	.470	23.0	3.49	.050	90.8
B (mg/kg)	4.12	<2	11.0	2.50	<2	21.5
Ba (mg/kg)	81.8	17.7	460	29.4	2.78	274
Be (mg/kg)	.120	<0.02	1.860	.430	<0.005	2.790
Bi (mg/kg)	.230	.050	2.610	.170	<0.02	6.790
Br (mg/kg)	<20	<20	280			
C (%)	39.6	8.67	51.0	1.45	.088	44.6
Ca (mg/kg)	4015	596	12900	869	25.0	7580
Cd (mg/kg)	.370	<0.01	2.22	.060	<0.02	.530
Co (mg/kg)	1.59	.330	40.1	4.99	<0.5	70.2
Cr (mg/kg)	6.34	<0.2	43.5	18.3	<1	168
Cu (mg/kg)	10.7	.850	1310	7.39	<0.5	63.7
Fe (mg/kg)	3840	809	31100	15300	557	98900
Hg (mg/kg)	.201	.043	.620	.023	<0.005	.175
K (mg/kg)	1040	413	4560	596	<100	13200
Li (mg/kg)	2.04	<0.4	25.4			
LOI (%)	75.2	<0.1	97.2			
Mg (mg/kg)	776	302	7310	2550	36.0	27200
Mn (mg/kg)	392	25.8	5160	129	3.59	1940

Mo (mg/kg)	.630	.230	10.8	.530	.030	10.3
Na (mg/kg)	74.6	<20	309	76.6	<50	561
Ni (mg/kg)	7.48	1.88	435	7.72	<0.5	212
P (mg/kg)	897	<30	2190	408	<50	2830
Pb (mg/kg)	36.4	5.00	657	7.18	1.11	39.3
Rb (mg/kg)	10.6	2.72	58.7	7.61	<0.01	130
S (mg/kg)	1550	329	37100	133	<50	11500
Sb (mg/kg)	.290	<0.02	4.34	.110	<0.02	.390
Se (mg/kg)	.250	<0.5	3.17	.480	<0.04	2.71
Si (mg/kg)	408	<0.1	1270			
Sn (mg/kg)	<0.5	<0.5	10.0	.700	<0.5	4.36
Sr (mg/kg)	26.4	6.81	88.4	5.93	<1	45.1
Th (mg/kg)	1.57	.150	20.7	3.51	<0.02	36.7
Ti (mg/kg)	272	50.6	2010	755	20.5	3510
Tl (mg/kg)	.210	.050	.770	.110	<0.03	.730
U (mg/kg)	.480	.070	4.31	1.32	.150	19.4
V (mg/kg)	12.7	3.18	77.5	26.9	1.00	184
Zn (mg/kg)	62.8	18.5	595	39.2	<3	361

Boron, Be, Se, and Sn were excluded from further statistical analysis: more than 50% of samples of B and Se had concentrations below the analytical detection limit (DL) in both humus and topsoil; 82% of Be results and 81% of Sn results in humus samples were below the DL.

Correlations between element concentrations in humus and minerogenic topsoil were evaluated by determining the Spearman rank correlation values; here, the total numbers of samples and the different soil parent materials were also considered. The correlation between the element concentration and the organic C content was additionally taken into account. Scatter plots of the element concentrations in humus and in minerogenic topsoil, and of the content of the element and the content of organic C, were elaborated where significant Spearman values were obtained.

The element concentration often showed a skewed data distribution in both sample media due to the presence of high extreme values. Thus, log-transformed data were used in further statistical analysis.

Minerogenic material is easily intermixed with decayed biogenic material in humus samples, especially if the humus layer is thin. Humus samples with less than 19% of carbon were identified as negative anomalies in box-and-whisker plots on a logarithmic scale. These humus samples were considered to be less representative than other humus samples due to the relatively high amount of minerogenic material, and they were examined separately in scatter diagrams. In the next step, histograms, box plots, and cumulative probability (CP) plots of the humus and topsoil log-transformed data, together with scatter

plots of log-transformed data (Fig. 4.2), were constructed for all samples using R Studio software.

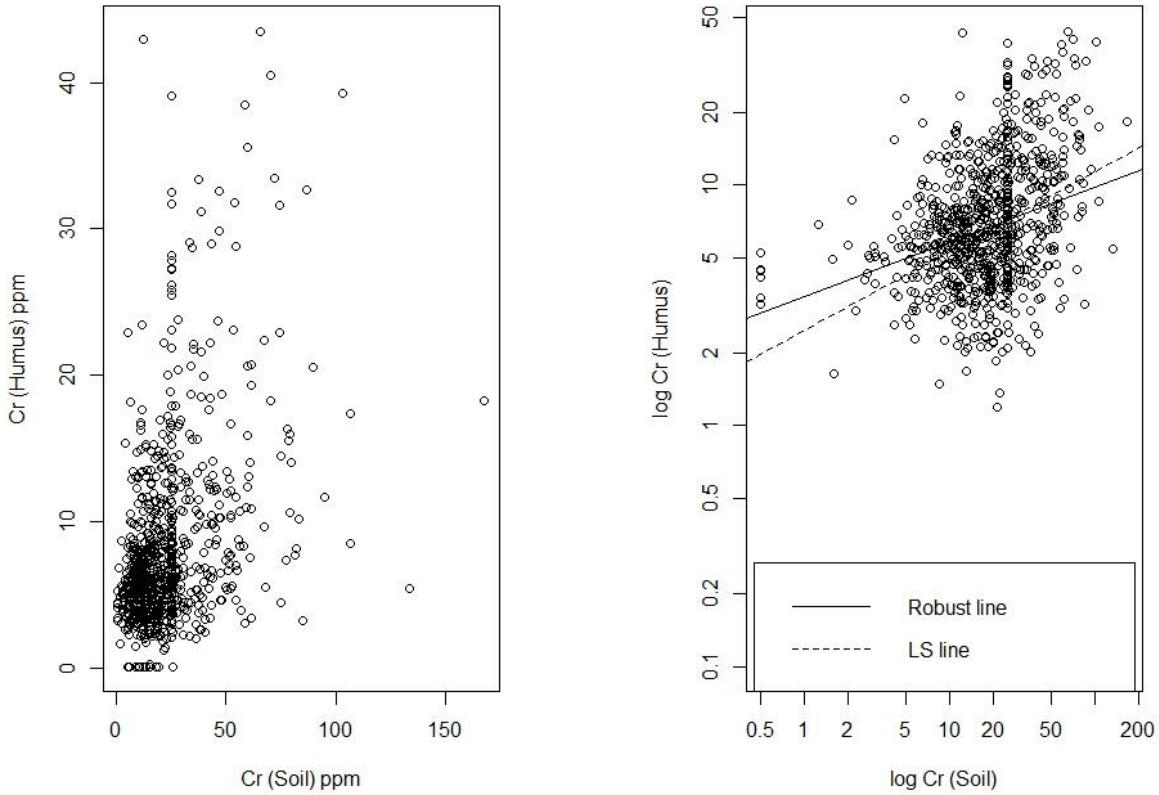


Fig. 4.2: *Scatter diagrams of the Cr concentration in topsoil (x-axis) and humus (y-axis) from the original data (on the left) and from log-transformed data (on the right) (fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus).The number of sample pairs is 816.*

The exploratory data analysis (EDA) approach was used here to map the humus and topsoil concentrations. Five intervals were established based on the quantiles of the distributions, and the maps were then elaborated by means of ArcGIS software.

4.4 Results and discussion

4.4.1. Element concentrations in humus and topsoil

According to the histograms, and in particular the CP plots and box plots, most elements have a completely different distribution of concentrations in humus and topsoil samples. It is clearly evident in the CP plots that the distributions of element concentrations in humus and topsoil are almost always completely separated, indicating totally different ranges of concentrations in these two sample media.

The only elements showing similar median concentrations were Bi, Mo, Na, Ni (Fig. 4.3), and Rb. The concentrations of some elements were much higher in humus than in topsoil, namely Ag, Ba, C, Ca, Cd (Fig. 4.4), Cu, Hg, K, Mn, P, Pb, S, Sb, Sn, Tl, and Zn. The humus median value was equal to or even higher than the upper whisker line of the topsoil distribution for Ca, Cd, Hg, P, Pb, S, Sb, and Sr. For Ag, Zn, and Cu, the median concentrations of humus and topsoil were more similar (Table 4.1), but the humus distributions showed evident breaks in the slope, reaching much higher values in humus (Table 4.1).

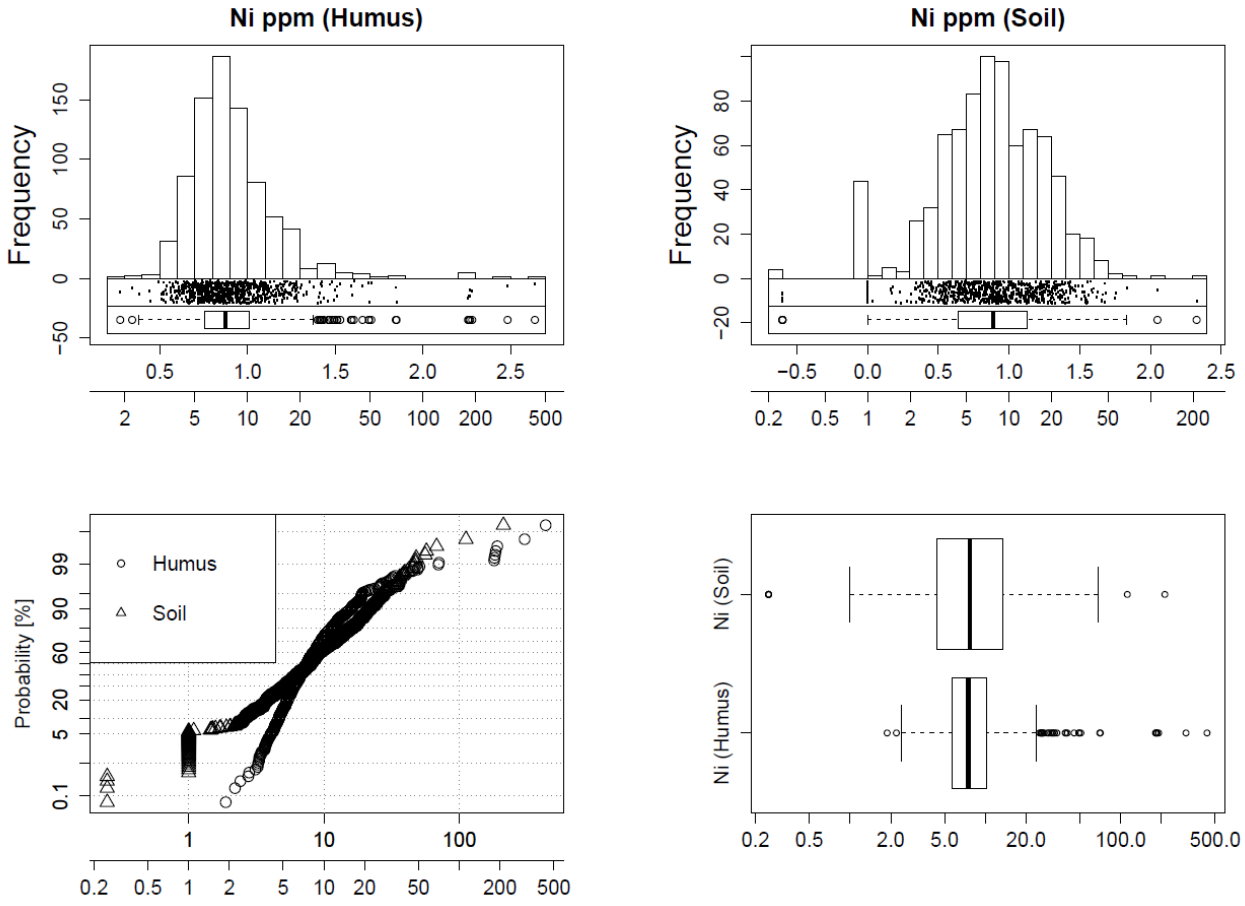


Fig. 4.3: *Example of histograms, CP plots and box plots for log-transformed data for elements (Ni) with similar medians in humus and topsoil(fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus). The number of sample pairs is 816.*

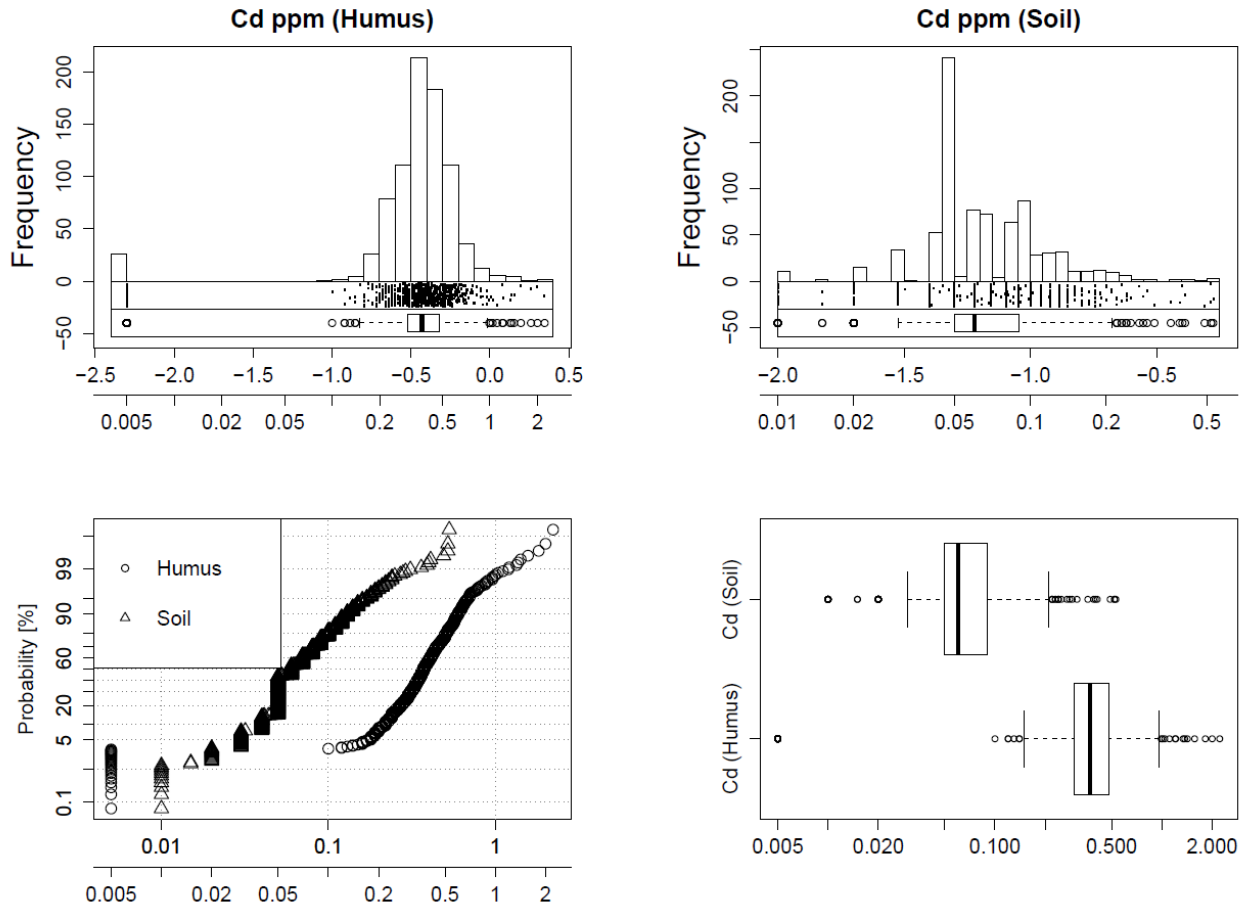


Fig. 4.4: *Example of histograms, CP plots and box plots for log-transformed data for elements (Cd) with higher concentrations in humus than in topsoil (fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus). The number of sample pairs is 816.*

The remaining analyzed elements, Al, As (Fig. 4.5), Co, Cr, Fe, Mg, Th, Ti, U, and V, had lower concentrations in humus than in topsoil. Of these, only Al, Fe and Th had much lower median concentrations in humus, corresponding to the lower whisker line in the topsoil distribution. Arsenic, Co, Cr, and Mg showed breaks in the slope in the CP plots of humus distributions, while the other elements (Al, Fe, Th, Ti, U, V) were log-normally distributed.

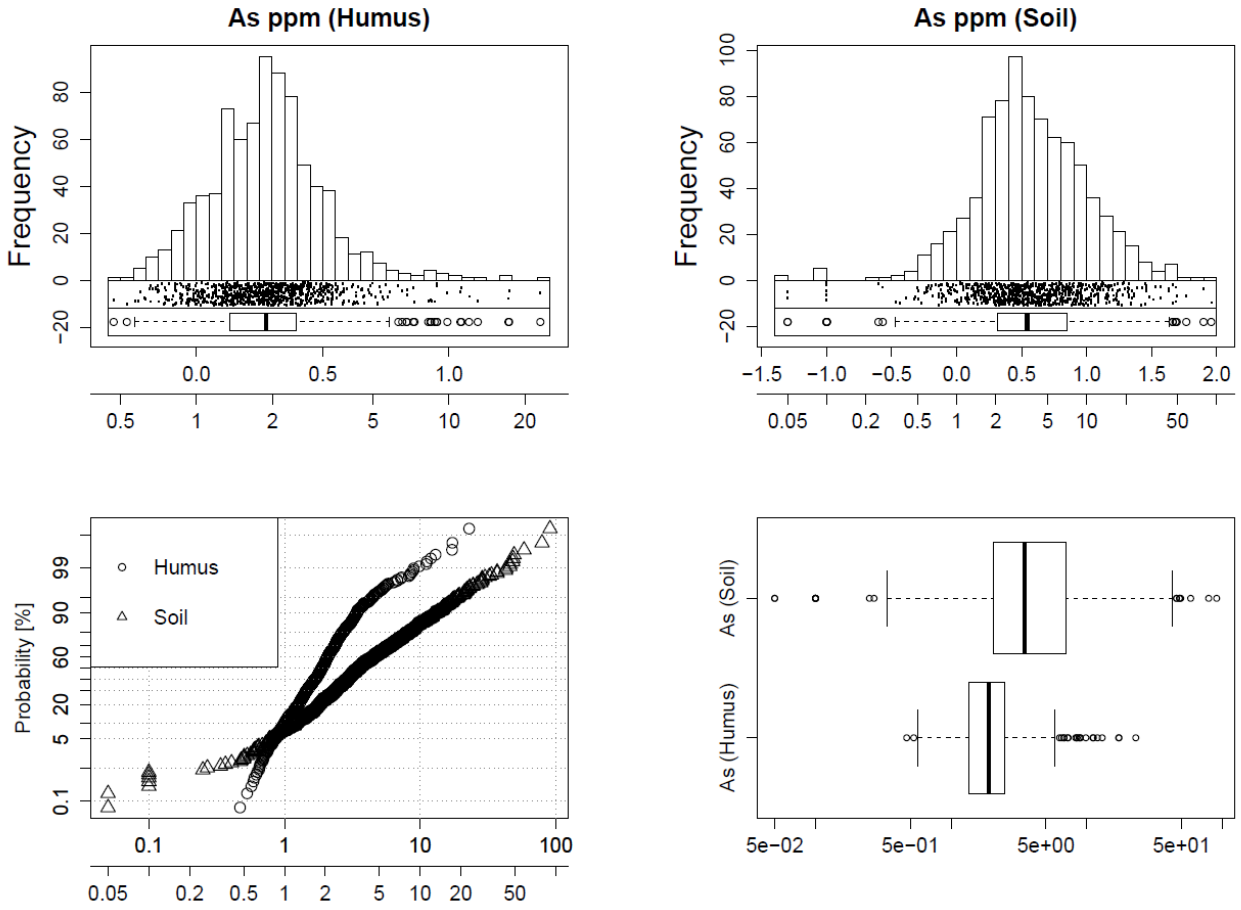


Fig. 4.5: *Example of histograms, CP plots and box plots for log-transformed data for elements (As) with lower concentrations in humus than in topsoil (fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus). The number of sample pairs is 816.*

4.4.2. Correlation between humus and topsoil

Even when the Spearman rank correlation values (Table 4.2a) were statistically significant, the scatter plots of the element concentrations in topsoil and humus clearly showed that the correlations were actually not significant. The significance of the Spearman rank correlation values can be explained by the presence of a few highly anomalous values and the large amount of data. However, only a few elements did not display a wide dispersion of the measured values in their scatter plots.

Table. 4.2. *a) Correlation coefficients between humus and topsoil samples for the selected elements from southern Finland sampled during 2002–2013. Number of sample pairs = 816. The correlations were computed using the Spearman method.* ** *= Correlation is significant at the 0.05 level (2-tailed);* * *= Correlation is significant at the 0.01 level (2-tailed; b) Correlation coefficients between selected elements and organic C content in humus samples from southern Finland during 2002–2013. Number of sample pairs = 816. The correlations were computed using the Spearman method.* ** *= Correlation is significant at the 0.05 level (2-tailed);* * *= Correlation is significant at the 0.01 level (2-tailed).*

a)

Element	Correlation coefficient (Spearman's ρ)
Ag	0.228**
Al	0.053
As	-0.009
Ba	0.546**
Bi	0.022
Ca	0.485**
Cd	0.102**
Co	0.434**
Cr	0.359**
Cu	0.236**
Fe	0.231**
Hg	0.114**
K	0.496**
Mg	0.530**
Mn	0.547**
Mo	0.271**
Na	0.163**
Ni	0.327**
P	0.247**
Pb	-0.18
Rb	0.299**
S	0.267**
Sb	-0.118**
Sr	0.431**
Th	-0.146**
Ti	0.342**
Tl	0.170**
U	0.176**
V	0.271**
Zn	0.476**

b)

Element (Humus)	Correlation coefficient (Spearman's ρ)
Ag	0.113*
Al	-0.780**
As	-0.429**
Ba	-0.150**
Bi	-0.192*
Ca	-0.037
Cd	0.310**
Co	-0.440**
Cr	-0.557**
Cu	0.150**
Fe	-0.756**
Hg	0.310**
K	-0.146**
Mg	-0.570**
Mn	-0.167**
Mo	-0.170**
Na	-0.567**
Ni	-0.112
P	0.240**
Pb	-0.181**
Rb	-0.401**
S	0.683**
Sb	0.269**
Sr	-0.106**
Th	0.211**
Ti	-0.620**
Tl	-0.074*
U	-0.540**
V	-0.552**
Zn	-0.083*

For some of the elements (Al, Ba, Ca, Fe, K, Mg, Rb, Sr, Ti, and Zn), the concentrations in humus were positively correlated with the concentrations in topsoil, especially in the sand parent material (Fig. 4.6). The concentrations of these elements in humus were often determined by the amount of minerogenic matter. Clay deposits are usually rich in these elements, and the dispersion of soil dust or challenges in humus sampling could lead to enrichment of mineral particles in the organic layer. The higher concentrations in humus samples, depending on the proportion of mineral matter in the samples, were thus negatively correlated with the contents of organic C in humus (Fig. 4.7). Negative Spearman rank

correlation values were recorded for all of these elements enriching in mineral soils (Table 4.2b). Anomalies for these elements, correlated with the amount of clay deposits, are also clear in the distribution maps.

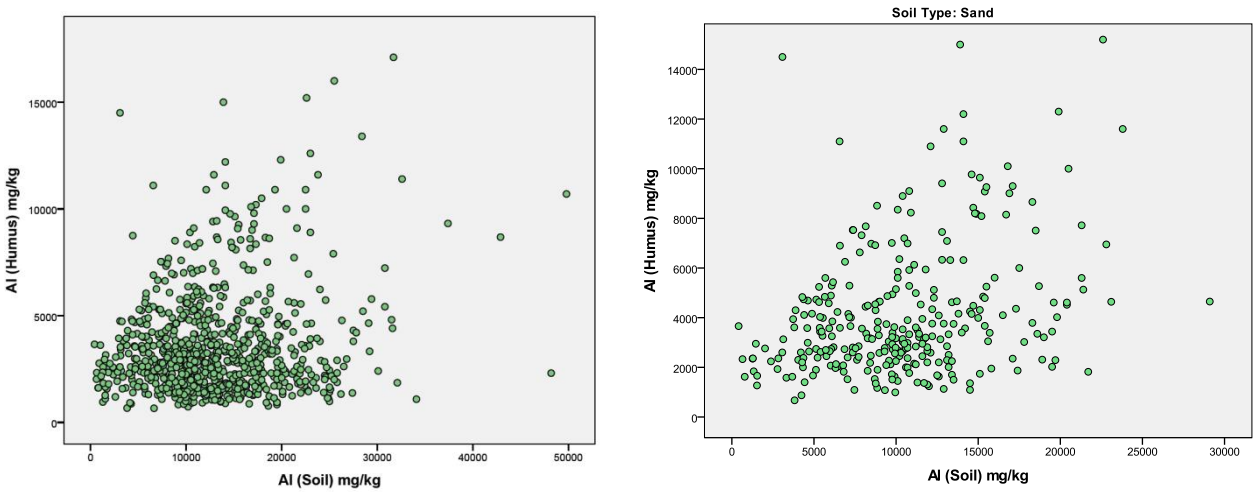


Fig. 4.6: *Scatter diagrams of the Al concentration in topsoil (x-axis) and humus (y-axis) samples (left) and in topsoil with sand soil parent material (x-axis) and humus (y-axis) (right) in Southern Finland during 2002 – 2013 (fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus). The number of sample pairs is 816.*

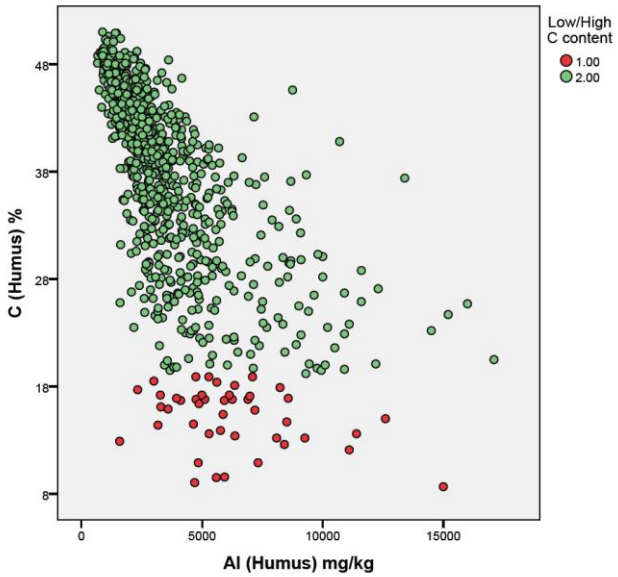


Fig. 4.7*: Scatter diagram of the Al concentration (x-axis) and organic C content (y-axis) in humus samples in Southern Finland during 2002 – 2013 (fraction size <2 mm, concentrated nitric acid leach). Red circles indicate humus samples with low organic C (less than 19%). The number of samples is 816.*

Other elements showed a different behavior, which could be explained by atmospheric deposition. Evident outliers, with probable anthropogenic origin, appear in the As, Bi, Cd, Co, Cu, Mo, Ni, and Pb scatter plots, and can be observed for some elements in Figures 4.8a–d. Scatter plots for Mn, Rb, Th, V, and Zn also show some outliers. The CP plots and the other statistical graphs display multimodal distributions in humus, with the outliers coincident with the high values observed in the scatter plots (Figs. 4.3, 4.4, and 4.5).

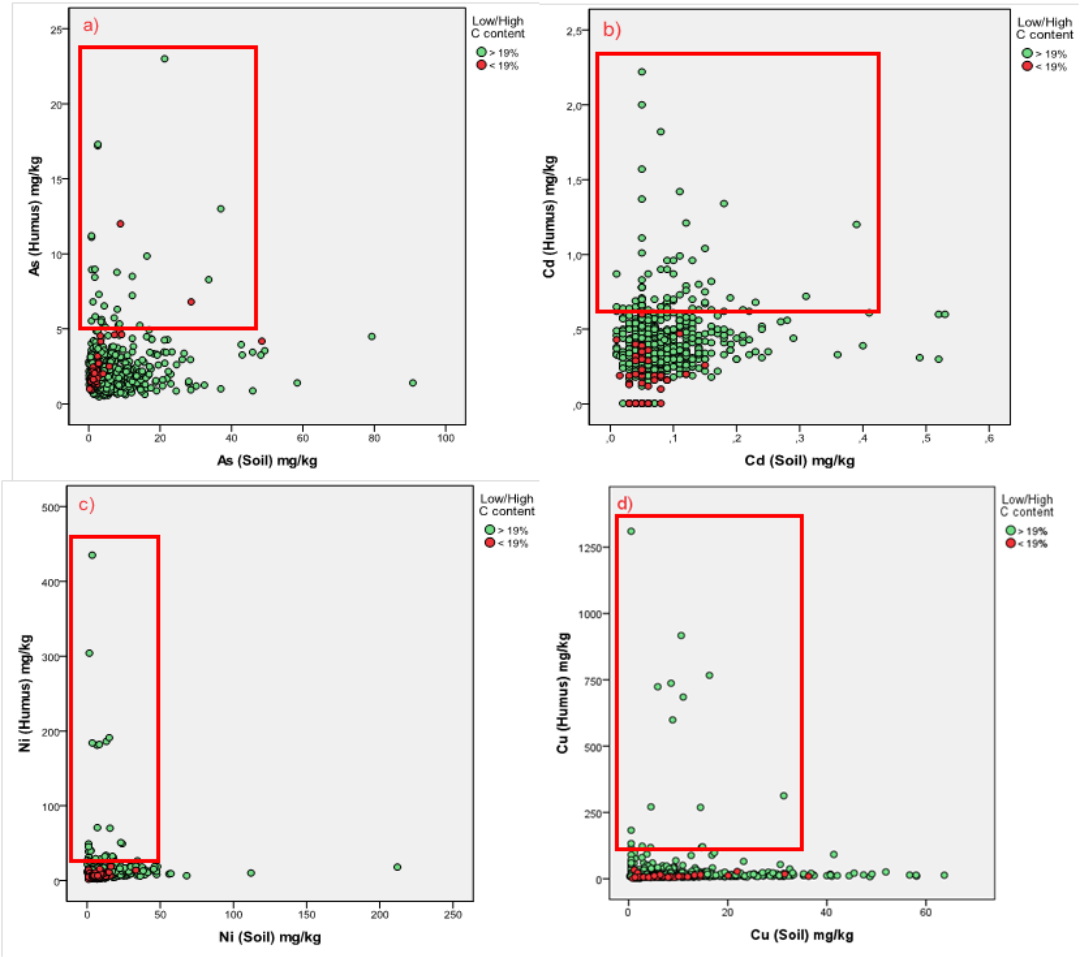


Fig. 4.8 *Scatter diagrams of As (a), Cd (b), Ni (c) and Cu (d) concentrations in topsoil (x-axis) and humus(y-axis) samples in Southern Finlandduring 2002 – 2013 (fraction size <2 mm, aqua regia extraction for topsoil and concentrated nitric acid leach for humus). The number of sample pairs is 816. The samples with high concentrations representing anthropogenic input are highlighted with red squares. Red circles indicate humus samples with low organic C (less than 19%).*

4.4.3. Deposition and concentrations in humus

In order to explain the anomalous high values in humus observed in the scatter plots and in the statistical graphs, with a probable anthropogenic origin, the geographic distributions of these elements in humus and topsoil were analyzed and then compared with the national deposition data obtained on moss compositions (Rühling 1992, 1994; Rühling and Steinnes, 1998; Salminen et al. 2004, 2011).

National surveys on heavy metal deposition have been carried out four times in Finland, in 1985, 1990, 1995, and 2000. The surveys formed part of the Nordic and pan-European surveys (Rühling et al., 1987, 1992, 1996; Rühling, 1994; Rühling and Steinnes, 1998). The concentrations of 10 elements (Cd, Cr, Cu, Fe, Ni, Pb, Zn, and V; and As and Hg since 1995) were determined using moss as a pollution bioindicator. Methods based on the use of mosses for surveying heavy metal deposition were developed in Sweden at the end of the 1960s (Rühling and Tyler, 1968; Tyler, 1970). Mosses are suitable bio-indicators because they obtain most of their nutrient supply directly from rainwater and from dry deposition (Poikolainen et al., 2003).

Further progress was made between 1999 and 2003, when multipurpose regional geochemical mapping was carried out between Finland, Russia, and Norway (Salminen et al., 2004).Terrestrial mosses, organic soil layers, stream waters, and C-horizon samples were collected from all over the mentioned regions, with an average sample density of one site per 1000 km^2 and the analysis of 48 elements, in order to define the anthropogenic impact. Salminen et al. (2004) found that anthropogenic factors can control the element concentrations in moss, and partly in stream waters and the organic soil layer, but not at all in the minerogenic soil layer. In mosses in southern Finland, the influence of airborne emissions of some elements transported over long distances can be detected, but the local sources have a stronger influence on the anomalies, especially in the organic layer. As an extension of this project, the distribution of element concentrations in terrestrial mosses and the organic soil layer was investigated in the Eastern Baltic region, an area surrounding the Gulf of Finland (Salminen et al., 2011).New moss and organic soil layer (humus) samples were collected from Estonia, Latvia, and Lithuania. Salminen et al. (2011) concluded that heavy metals detected in organic soil include fingerprints of older emissions from local industries. In the context of the Barents Ecogeochemistry project, during 2000–2001, 786 humus (0–3 cm layer) samples were collected, and 177 samples in the Baltic countries in 2003, in order to study the situation resulting from the Chernobyl fallout in 1987.The results show that the fallout can still be detected in the uppermost humus layer in North East Europe (Ylipieti et al., 2008). Saxén and Ilus, (2008) have shown that most of the Chernobyl Cs is found in the litter and uppermost humus layers compared to the underlying mineral soil layers . It must be noted here that in the geochemical studies the organic layer is often divided in litter and humus layer (Saxén and Ilus, 2008). In the study presented in this paper, as well as in the Barents Ecogeochemistry project, the samples presented are composed exclusively of the humus layer the litter being removed.

According to Rühling and Steinnes (1998), two local heavy metal pollution sources dominate in Finland, the copper-nickel smelter at Harjavaltaon west coast and the steel mill at Tornio in northwestern Finland. Their impact is evident as elevated Cd, Cu, and Ni concentrations in mosses, even regionally. The oil refineries at Naantali on the southwest coast and Porvoo in south cause locally elevated Ni and V concentrations in mosses (Rühling and Steinnes, 1998). The Pori-Harjavalta smelter and the Porvoo area are included in the studied area introduced in this paper.

Elevated Ag and Bi concentrations in the organic layer and As, Cu, and Ni concentrations in both the organic layer and moss have been detected in the Harjavalta smelter area in previous studies (Salminen et al., 2004, 2011). The elements were considered to be enriched in these layers due to the copper-nickel smelters (Salminen et al., 2011).

Lead, V, and Cd are the elements most affected by long-range transport from central Europe to the southwestern part of Finland, showing a decreasing gradient from south to

north in mosses. Cadmium, however, also shows locally elevated concentrations around Harjavalta (Rühling and Steinnes, 1998).

Arsenic, Fe, V, and Zn concentrations additionally display a decreasing gradient from south to north in moss, mostly being determined by the urban, densely populated, and industrial areas, with intensive traffic (Salminen et al., 2011).

Examining the element distribution maps of the study presented in this paper, the differences between the humus and topsoil distributions are immediately obvious from the enormously different scale for the topsoil maps (Figs 4.9–4.12). The topsoil element distributions show a strong relationship with the bedrock geology (Figs 4.10 and 4.12). The Ni distribution in topsoil is clearly related to the Ni-Co-Cu metallogenic area of the Tampere Region (Fig.4.10). On the contrary, the humus concentration distributions show a strong correlation with the anthropogenic impact of known deposition from local pollution sources (Figs 4.9 and 4.11).

High anomalies in humus samples in the Pori-Harjavalta region are evident in the maps for Ag, As, Bi, Cu, Cd, and Ni (Fig. 4.9), corresponding to the lowest values in the soil distribution map (Fig.4.10). The Mo, Pb (Fig. 4.11), V, and Zn maps reveal major deposition in the most industrialized and urban areas, probably due to the combustion of coal, oil, and the form erly leaded fuel. Lead concentrations in humus (Fig.4.11) are generally higher than in topsoil (Fig.4.12), partly due to long-range transport, but with anomalies in three areas: the large Metropolitan Area of Helsinki, the surroundings of the Harjavalta smelter, and the city of Tampere. The map of molybdenum distribution indicates anomalies in humus layer in the Harjavalta and Porvoo regions. Anomalies of V and Zn in humus are found in the Tampere Region.

According to Salminen et al. (2011), Co, Rb, and Th anomalies in humus in the Eastern Baltic region have a geogenic origin. In southwestern Finland, a high anomaly coincides with a polymetallic anomaly detected in many elements due to hydrothermal processes in the upper crust. In the realized maps, the anomalies in humus are found in the Tampere Region and the Porvoo area for Rb, in the Espoo area for Th, and in Harjavalta, the Tampere Region, and the Helsinki Metropolitan Area for Co.

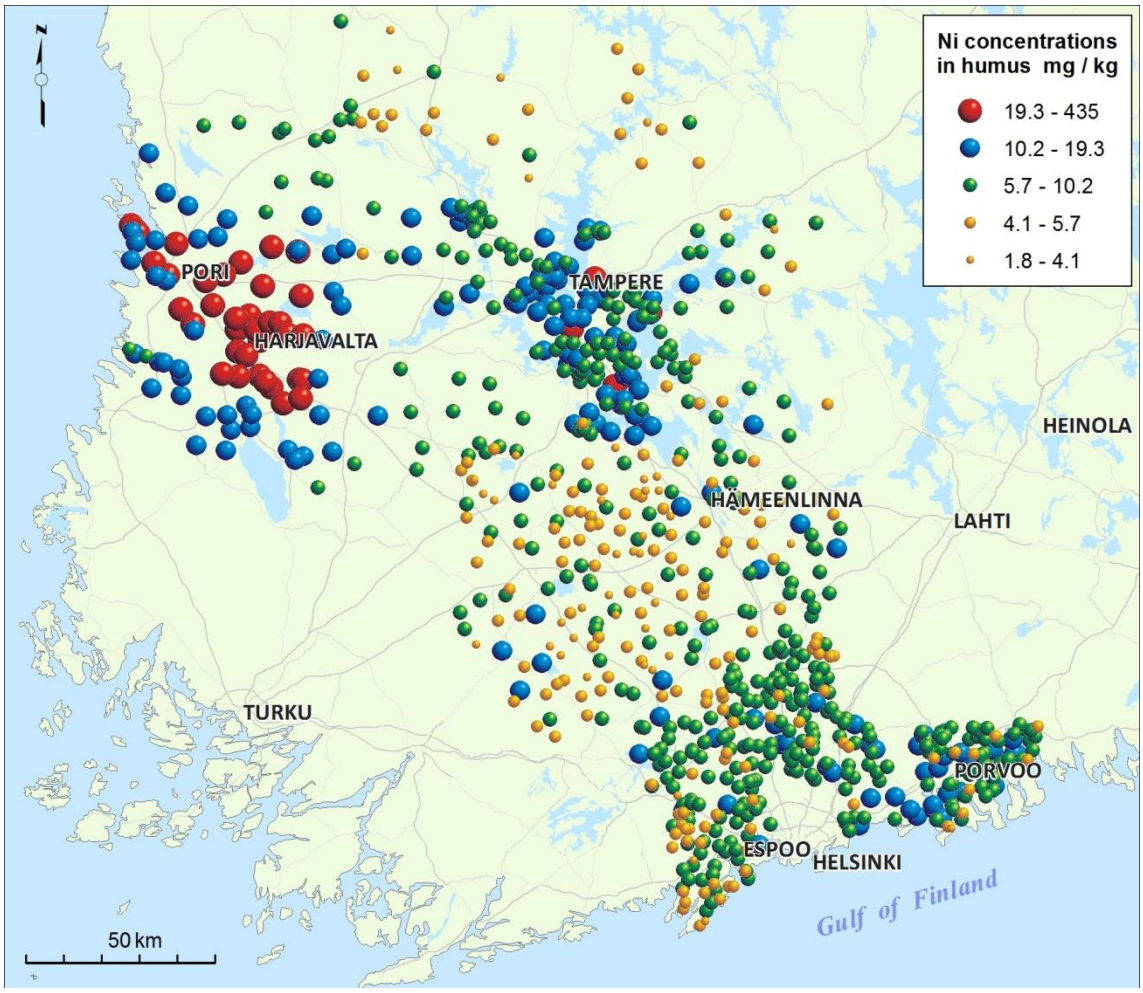


Fig. 4.9: *Distribution of Ni in humus samples. Red dots: high anomalies; blue dots: values between 75th percentile and upper Whisker line; green dots: values between 25th and 75th percentile; yellow dot: values below 25th percentile; small yellow dot: small anomalies. The number of samples is 816. Ni shows the highest positive anomalies in the western part of the mapping area, partly explained by the deposition from the copper-nickel smelter at Harjavalta. Topographic map © National Land Survey of Finland and ICT Agency HALTIK.*

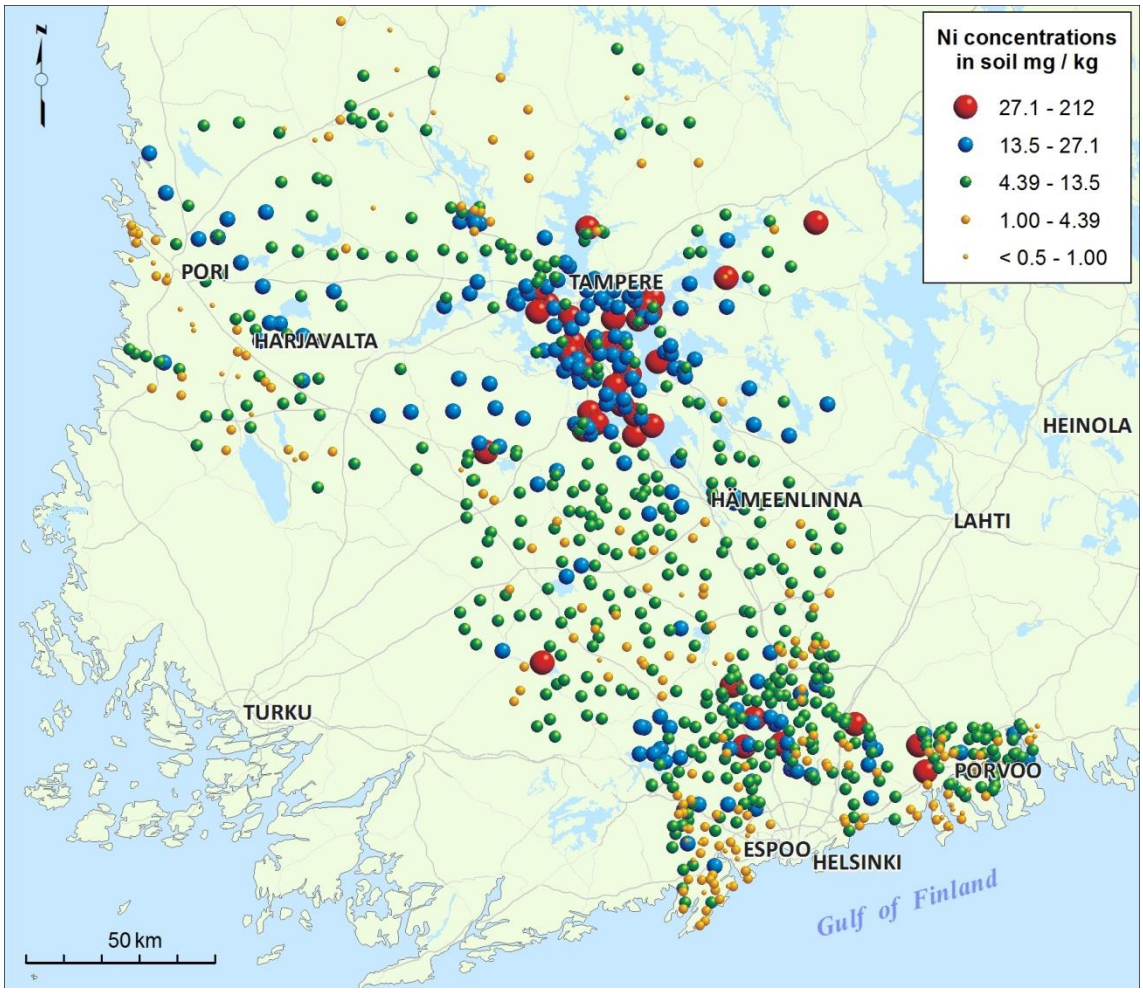


Fig. 4.10: *Distribution map of Ni in topsoil samples. Red dots: high anomalies; blue dots: values between 75th percentile and upper Whisker line; green dots: values between 25th and 75th percentile; yellow dot: values below 25th percentile; small yellow dot: small anomalies. The number of samples is 816. Topographic map © National Land Survey of Finland and ICT Agency HALTIK.*

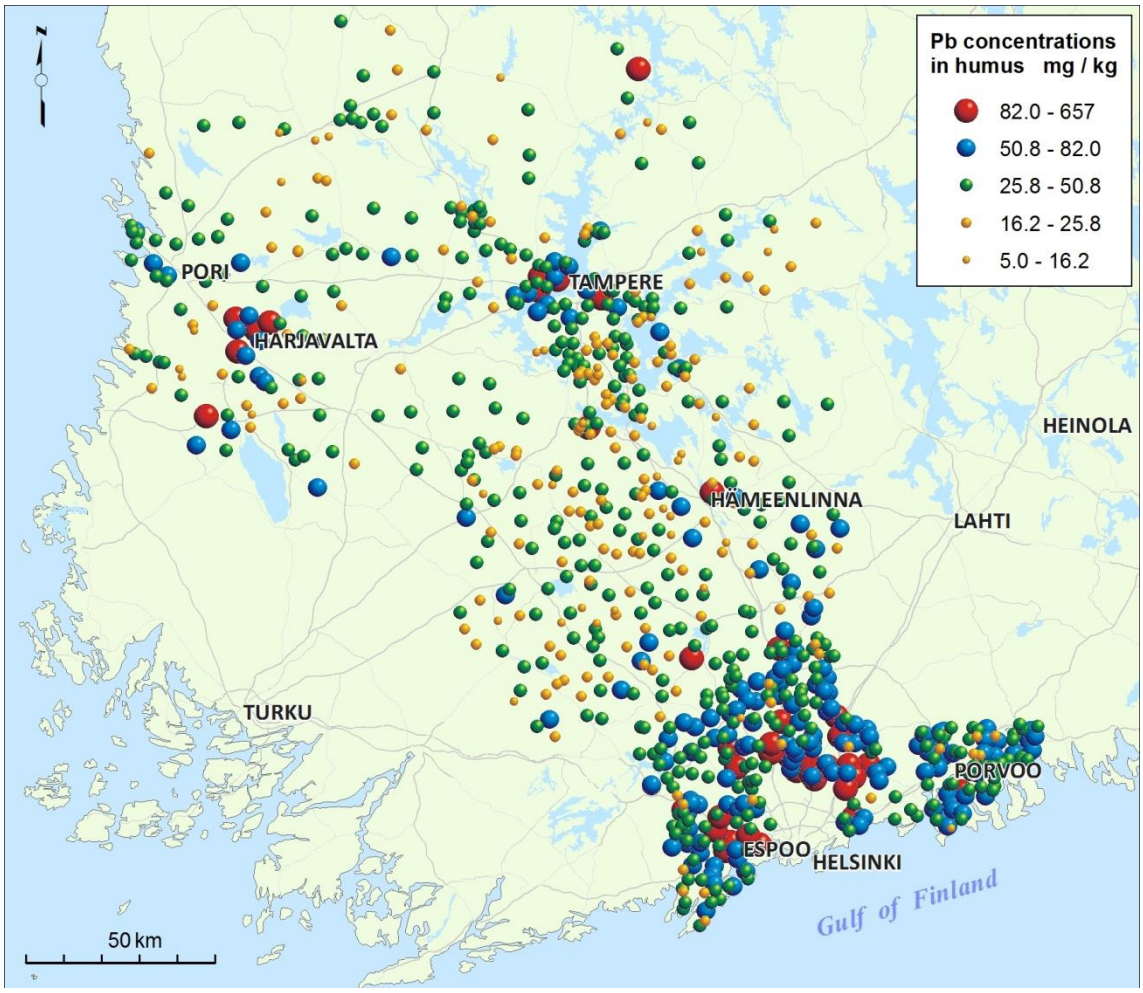


Fig. 4.11*:* *Distribution of Pb in humus samples. Red dots: high anomalies; blue dots: values between 75th percentile and upper Whisker line; green dots: values between 25th and 75th percentile; yellow dot: values below 25th percentile; small yellow dot: small anomalies. The number of samples is 816. Pb shows the highest positive anomalies around the urban areas of Helsinki, Porvoo and Tampere. Topographic map © National Land Survey of Finland and ICT Agency HALTIK.*

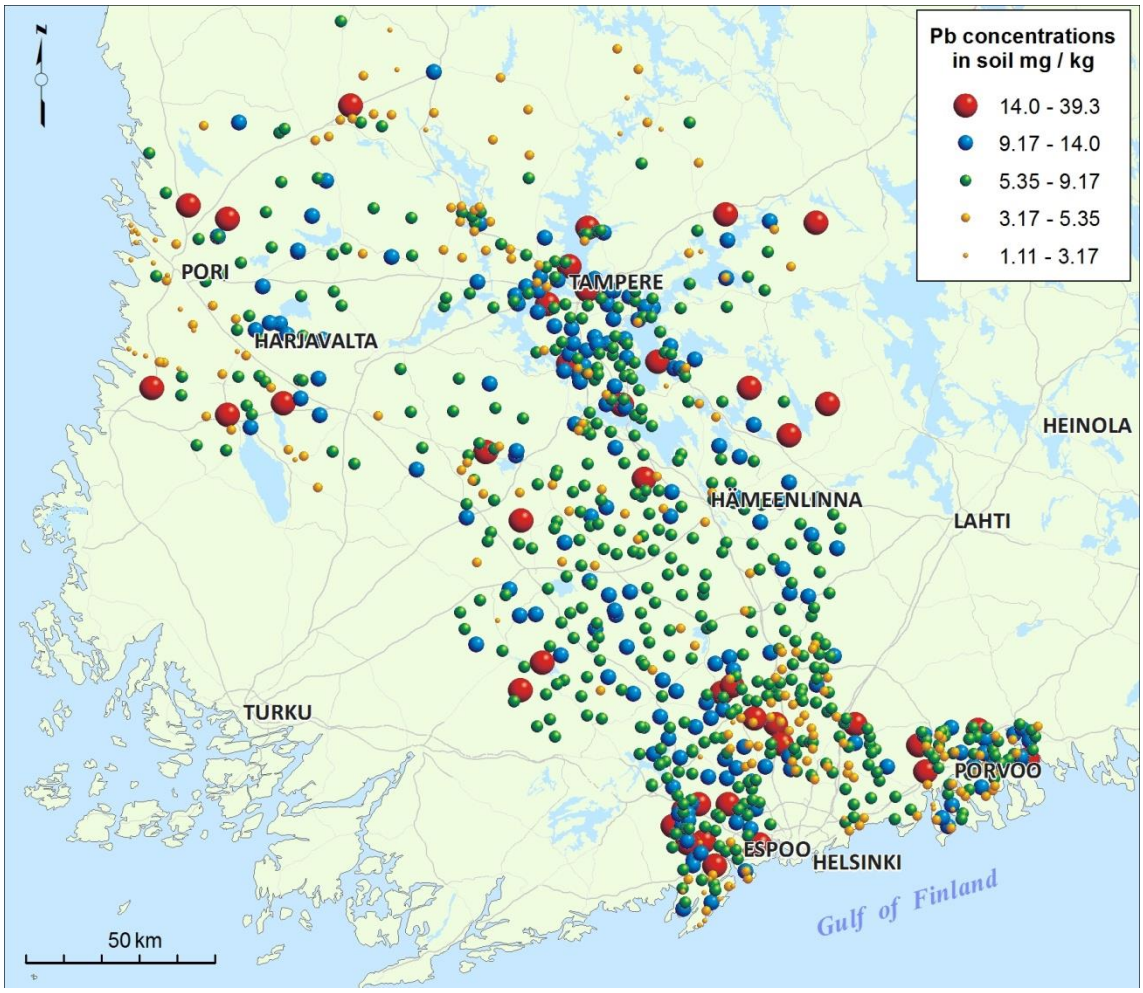


Fig. 4.12*: Distribution of Pb in topsoil samples. The number of samples is 816. Red dots: high anomalies; blue dots: values between 75th percentile and upper Whisker line; green dots: values between 25th and 75th percentile; yellow dot: values below 25th percentile; small yellow dot: small anomalies. Topographic map © National Land Survey of Finland and ICT Agency HALTIK.*

4.5 Conclusions

According to the literature, humus samples reflect the interplay between the atmosphere, biosphere, and lithosphere. Looking at the results presented here, based on 816 humus and topsoil samples from southern Finland, the humus concentrations are more affected by the atmospheric impact than by the lithogenic contribution. In contras to the common view of the similarities between the topsoil and uppermost organic layer, the statistical analysis carried out here already provides an initial idea of the considerable differences between humus and topsoil concentrations for almost all of the analyzed elements.

The differences were confirmed by the analysis of correlations between the humus and topsoil concentrations. A vague positive trend was only detected for some elements, accompanied by negative correlations of the element concentrations in humus with the organic carbon content. This indicates that the concentrations of these elements, such as K, Mg, Fe, and Al, in humus samples are determined by the content of mineral matter, derived from soil dust. Visible anomalies in the distribution maps of the same elements can be

observed where the clay deposits are more diffuse. Some anomalies also appear in the large Helsinki Metropolitan Area. Here, the humus samples are often not very representative due to their high content of minerogenic material. This is partly due to the difficulty in collecting representative humus samples, as the organic layer is very thin and mixing with minerogenic material is common. In the southernmost parts of Finland, the humus layer is young and not as well developed, since the thickness of overburden sediments is rather thin. Podzol soils are not as common as in other parts of the sampling area.

Concentrations of other elements, such as Cu, Ni, and Pb, are often controlled by atmospheric deposition. Their distribution maps were compared with national moss data (see references). High values were recorded in areas where the anthropogenic impact is high, such as the Harjavalta area, where older emissions from the smelter still cause anomaly patterns for some elements, and in the more densely populated and industrialized areas, such as the city of Tampere and the coastline from Porvoo to Helsinki.

This study revealed that the long-term anthropogenic influence on humus concentrations, causing locally high anomalies, can even be observed many years after the local point-source emissions have decreased. The potential impact of long-range transport was not clearly identified, although the enrichment of potentially toxic elements related to human activities rather than the geological environment in humus was found in more densely populated and industrialized areas. In order to obtain a more precise and detailed view of the anthropogenic impact on the quality of the humus layer, further humus samples should be collected with a sufficient sampling density close enough to city centers and industrialized areas. This will also improve knowledge of humus behavior and anthropogenic inputs to the topmost layer of the ground surface providing tools and more precise background information for better assessment of potential risks to the environment and human health.

Chapter 5 – Other activities

5.1 Follow-up geochemical survey in Caserta area

Together with the follow-up survey in the potentially hazardous area between Avellino and Salerno, another follow-up sampling was carried out during the spring-summer seasons of 2015. The chosen area is located in north of Caserta city, covering 144 km^2 of mainly forested land, interspersed with sparse agricultural and urban localities. The area is part of the, so called, "Terra dei fuochi", a wide intensely polluted territory in the Caserta province. In the potential hazard map of the Campania region, a small circle showed an area with a medium-high potential hazard, characterized by the contemporary presence of 6 potential hazardous elements. In the final risk map, the resulting risk in the same zone was very low or, at least, low. The high potential hazard makes it an important area to be analyzed, and the results can be an instrument to validate the human health risk assessment method here proposed. With a sampling density of 1 sample/4 km^2, 31 topsoil samples were collected (Fig.5.1). The statistic and cartographic elaborations are not presented in this work, due to the low number of samples.

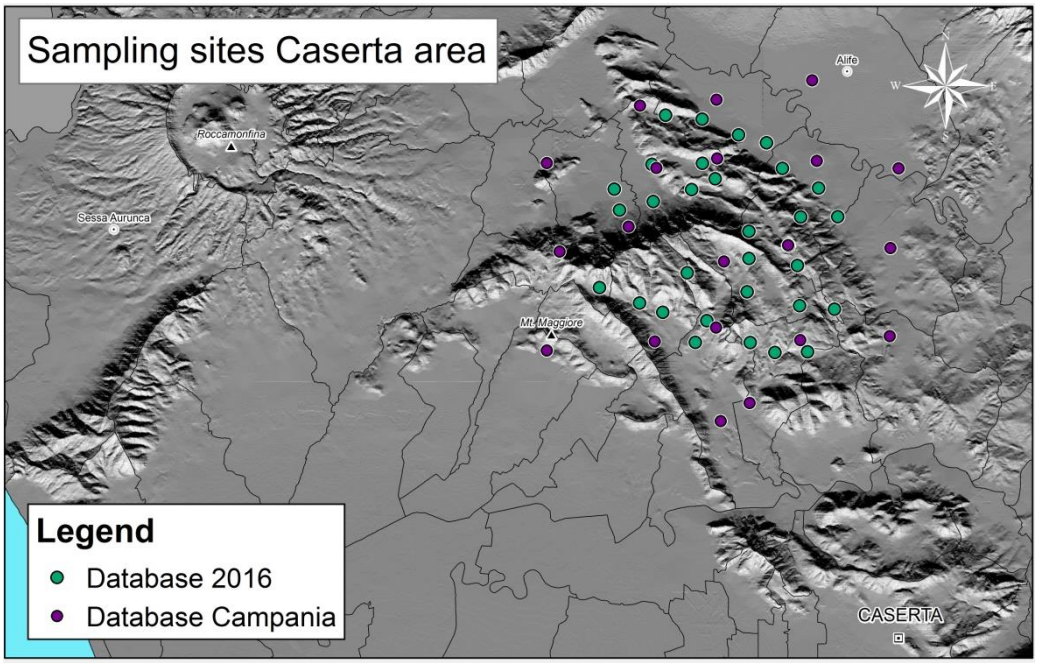


Fig. 5.1*: Sampling sites of Caserta area.*

5.2 Geochemical Atlas of Napoli and Salerno Gulfs marine sediments

From 2000 several geochemical surveys were carried out in Napoli and Salerno Gulfs, focusing both on inorganic and organic contaminants that lead to the publishing of different papers (e.g. Menghan W., 2014 and references therein). More samples were recently

collected in the Gulf of Napoli, in particular in the Trentaremi bay, located in a famous protected natural reserve (Archaelogical Park of Gaiola), close to Bagnoli site. The new samples were added to the old database and new statistic and cartographic elaborations have been carried out. These will be soon part of the new Geochemical Atlas of the Marine Sediments in Napoli and Salerno Gulfs.

The main difference with the usual topsoil analysis, concerns the investigation of organic pollutants as well. Harmful organic compounds, as the inorganic ones, exist in the environment independently from human activities, but higher input occurred after the industrial revolution. The most studied category of organic pollutants is POPs (Persistent Organic Pollutants) (Jones and De Voogt, 1999), including some of the most harmful compounds, such as Polycyclic Aromatic Hydrocarbons (PAHs), Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs). POPs exhibit the following characteristics: 1) high toxicity: small quantity of POPs may cause severe damage; 2) persistency; 3) accumulation: POPs accumulate in soil, sediment and biological adipose tissue; 4) mobility: most POPs are semi-volatile and they easily migrate in the atmosphere (Kukkonen et al., 2003).

5.2.1 Study area

Naples and Salerno Gulfs are located along the Eastern Tyrrhenian Sea, and are divided by Sorrento peninsula. Naples Gulf is semi-closed by Ischia and Procida islands in NW, Campi Flegrei and Campanian plain in NE, and Sorrento peninsula in SE, while Salerno Gulf locates on the coastal area offshore of Sele plain.

As already mentioned, the Tyrrhenian Sea is the result of Miocene-Quaternary extension contemporary with the eastward accretion and anticlockwise rotation of the Apenninic folds and thrust belt during the roll-back of the subducting Adria plate (Bruno et al., 2003; Insinga et al., 2008; Milia and Torrente, 1999; Sacchi et al., 2005). The Campanian Plain and Naples Gulf, as well as Sele Plain and Salerno Gulf, are parts of half-graben basins developed in eastern Tyrrhenian margin (Sacchi et al., 2005).

Sea floor of Naples and Salerno Gulfs are covered by Plio-Quaternary sedimentary and pyroclastic fall deposits (Bruno et al., 2003). Two small coalescent deltas, Sebeto delta and Sarno delta, characterize the eastern depositional system of Naples Gulf (Insinga et al., 2008). Along Sorrento peninsula, Capri Island and Salerno Gulf, Mesozoic-Cenozoic carbonate units also influence the composition of surface sediment (Milia and Torrente, 2003).

Volcanic process during the late Quaternary has significant influence on morphology and deposits in Naples Gulf (Aiello et al., 2005; De Vivo et al., 2001; Milia and Torrente, 2007; Milia and Torrente, 1999, 2003). Several volcanic eruptions occurred in Campania Plain (Campi Flegrei, Ischia and Mt Somma-Vesuvius) during Quaternary, producing among others, Campanian Ignimbrite 39 ka B.C (De Vivo et al., 2001) and Neapolitan Yellow Tuff 12 ka B.C. (De Vivo et al., 2010).

The natural and archaeological beauty of Naples and Salerno provinces, make the Campania region one the most touristic regions around Mediterranean Sea. The port of Naples has one of the highest level of passengers flow in the Mediterranean sea, and Naples is a junction for most of the transports in south Italy, including railway, and highway. Agriculture is still the basic income of economy, being recently partially replaced by service industries. Various stream system in Campania plain and Sele plain carry related products and fertilizers into the sea (Albanese et al., 2007).

Bagnoli area is one of the largest brownfield sites in Italy. It has been dismissed in the early 1990's. The area used to concentrate various industries, such as steel factory, asbestos materials manufacturing, cement and fertilizer production factories. Although it has undergone a large remediation programme funded by Italian Government, the area is still affected by high concentrations of toxic metals and organics (POPs, namely PAH, PCB and OCP) spreaded both in soil and in sea sediments of Pozzuoli Gulf (Albanese et al., 2010; De Vivo and Lima, 2008).

5.2.2 Sampling and sample preparation

Sediments samples derived from three different surveys: a general survey of sea sediments in Naples and Salerno Gulfs, for providing regional information; geochemical survey of Bagnoli site; geochemical survey of ports around Naples Gulf. Differential global positioning system (DGPS) was used to identify each location precisely.

The CNR Istituto Geomare Sud Naples collected sediment samples from 226 locations in Naples and Salerno Gulfs, following the directives of the national program for assessment of marine pollution of highly contaminated Italian coastal areas. In May 2000, 33 samples were collected using a box-corer with an inner diameter of 25 cm, while other 75 were collected by grab.

Bagnoli samples were collected by ICRAM between November 2004 and March 2005, including surface sediments (0-20 cm) of 123 boreholes along the Bagnoli coastline. Surface sediments (0-20 cm) in port of Naples were sampled by 11 boreholes by Norwest Italia S.r.l, investigating different harbor area of Campania region during the 2003 summer.

From May to July 2011, 186 samples (surface and bottom) had been subset in Geomare CNR Institute (Naples), including 35 box corer sediment samples and 80 grab sediment samples. Most of box core samples were divided into two parts, surface (or subsurface) and bottom sediment, as well as some of grabbing samples. Each sample were subset into three parts, 30g for metal and inorganic analysis, 100g for organic analysis and rest were stored in Geomare as backup.

In this study, 226 surface samples from the described surveys have been analyzed.

5.2.3 Chemical analysis and quality control

5.2.3.1 Inorganic Elements

All the Naples and Salerno Gulf, and Port of Naples sea sediments, after being air dried, were sieved and 30 g of the <150 μm fraction was retained for analysis of 53 elements. Analyses were carried out by ACME Analytical Laboratories Ltd. (Vancouver, Canada). Each sample was digested in a modified aqua regia solution and analyzed by inductively coupled plasma–mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES). Specifically, a 15-g split of the pulp was digested in 45 ml of the aqua regia mixture (1 part concentrated hydrochloric acid to 1 part nitric acid to 1 part deionised water) at 90 °C for 1 h. The solution was taken to a final volume of 300 ml with 5% HCl. Aliquots of sample solution were aspirated into a Jarrel Ash Atomcomp 975 ICP-Emission Spectrometer and a Perkin Elmer Elan 6000 ICP-Mass Spectrometer.

Precision of the analysis was calculated using three in-house replicates, and two blind duplicates submitted by the authors. Accuracy was determined using ACME's in-house reference material, DS2 (HMTRI, 1997).

Analyses of elements (Al, As, Be, Cd, Co, Cr, Fe, Hg, Mn, Ni, Pb, Cu, Sn, V, and Zn) of Bagnoli sites sediments were performed by ICRAM Laboratories. Microwave assisted acid digestion for a total decomposition of matrices was applied to sediment samples according to EPA Method 3052 (US-EPA, 1996). Each sample was digested in an HCl and HNO3 (1:3) solution for 15 min. The sample was placed in an inert polymeric vessel, sealed and heated in a microwave system. A 4-step heating cycle was performed prior to adding HF to the cooled solution. After a second heating cycle, H3BO3 was added to the solution. Finally, the solution was filtered and brought to a final volume of 100 ml with the addition of ultrapure water. As, Cd, Cu, Pb and Zn were analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry), Hg (and other elements, if characterized by concentrations below the ICP-OES detection limits) were analyzed by AAS (Atomic Absorption Spectroscopy).

5.2.3.2 Polycyclic Aromatic Hydrocarbons (PAHs) and Organochlorine Pesticides (OCPs)

PAHs and OCPs in sediments were concentrated to 0.2 ml under a gentle nitrogen stream and analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). The analysis was carried out in Key Laboratory of Biogeology and Environmental Geology of the Ministry of Education (Wuhan, P.R.C).

PAHs

The sediment samples from Naples and Salerno Gulfs were homogenized and frozen-dried. 10 g of dried sediments from each sample were spiked with 1000 ng (5μl of 200 mg l^{-1}) of recovery surrogates (naphthalene-D8; acenaphthene-D10; phenanthrene-D10; chrysene-D12 and perylene-D12) and were Soxhlet-extracted (4-6 cycles/h) with

dichloromethane for 24 h. Elemental S was removed by adding activated Cu granules to the collection flasks.

The sample extract was concentrated and solvent-exchanged to hexane and further reduced to 2-3 ml by a rotary evaporator (Heidolph4000). A 1:2 (v/v) alumina/silica gel column (both 3% deactivated with H_2O) was used to clean up the extract and PAHs were eluted with 30 ml of dichloromethane/hexane (3:7). The eluate was then concentrated to 0.2 ml under a gentle nitrogen stream. 1000 ng (5 μl of 200 mg l^{-1}) of hexamethylbenzene was added as an internal standard prior to gas chromatography- mass spectrometry (GC- MS) analysis.

PAHs were identified and quantified on a HP5972A GC-MSD following the QA/QC requirements of USEPA method 610. A standard mixture of 16 priority PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)-fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(ghi)perylene (Ultrascientific Co.) was used as a calibration solution. In the sample preparation, extracts and all fractions containing PAHs were concentrated to near dryness and constant weight for 24 hours and weighed. Prior to GC and GC-MSD injection, 2 μg of hexamethylbenzene were added to each sample as an internal standard. Detailed procedures of extraction, separation and analysis of PAHs in sediments can be found elsewhere (Chen et al., 2011).

For PAHs determinations of Bagnoli sites samples, the description is available in Albanese et al. (2010).

OCPs

The sediment samples were homogenized and frozen-dried. Fifteen grams of dried material from each sample were spiked with 20 ng of TCmX and PCB209 as recovery surrogates and were Soxhlet-extracted with dichloromethane for 24 h. Elemental S was removed by adding activated Cu granules to the collection flasks.

The sample extract was concentrated and solvent exchanged to hexane and further reduced to 2–3 ml by a rotary evaporator (Heidolph 4000). A 1:2 (v/v) alumina/silica gel column (both 3% deactivated with H_2O) was used to clean up the extract and OCPs were eluted with 30 ml of dichloromethane/hexane (2:3). The eluate was then concentrated to 0.2 ml under a gentle nitrogen stream. Twenty nanograms (4 μl of 5 mg l^{-1}) PCNB was added as an internal standard prior to gas chromatography–electron capture detector (GC-ECD) analysis.

OCPs were identified and quantified on a HP6890 GC-MSD following the QA/QC requirements of China Geological Survey (DD2005-1 and DD2005-3). A standard mixture of 26 OCPs including *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDD, *o,p′*-DDD, *p,p′*-DDE, *o,p′*-DDE, *α*-HCH, *β*-HCH, *γ*-HCH, *δ*-HCH, HCB, aldrin, dieldrin, endrin, *α*-Endosulfan, *β*-Endosulfan, *Trans*-chlordane, *Cis*-chlordane, endosulfan sulfate, endrin aldehyde, endrin ketone,

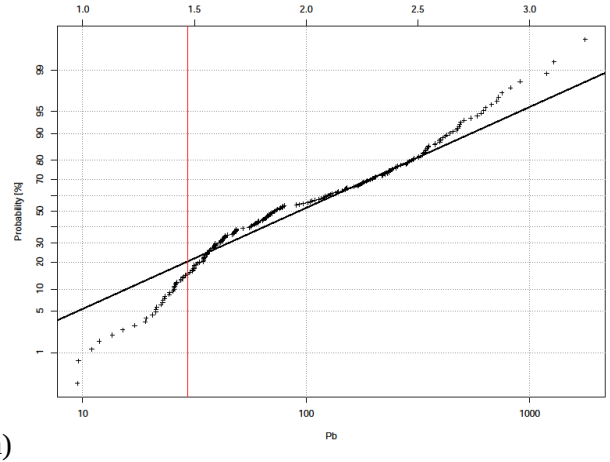
heptachlor, heptachlor epoxide, *Trans*-Nonachlor, *Cis*-Nonachlor and methoxychlor (Ultrascientific Co) was used as calibration solution. In the sample preparation, extracts and all fractions containing OCPs were concentrated to near dryness and constant weight for 24 hours and weighed. Prior to GC and GC-MSD injection, Twenty nanograms (4 µl of 5 mg l^{-1}) PCNB were added to each sample as an internal standard. Detailed procedures of extraction, separation and analysis of OCPs in sediments can be found elsewhere (Chen et al., 2011).

5.2.4 Statistic and cartographic elaborations

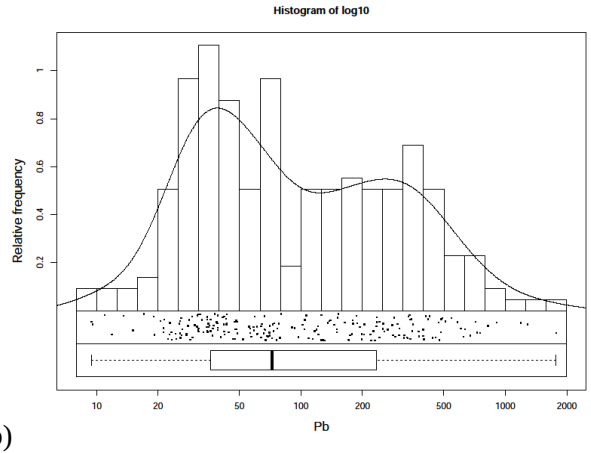
The database has been organized considering exclusively the analysis made on the surface samples. R software was used for the statistical analysis, elaborating CP plots, and a combination of several graphics, like histograms and box plots (see Chapter 3.4).

Dot maps, interpolated maps, *background/baseline* maps and the overcoming of the CSC threshold values were elaborated for all the metals, PAHs and OCPs (see Chapter 1.6 for the description of the methods).

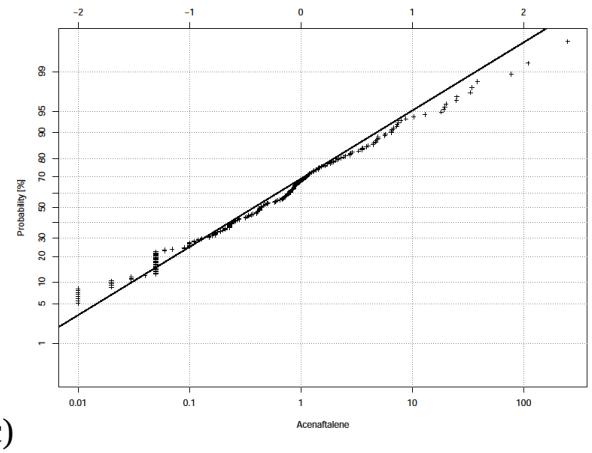
In the following section I show, as an example, the statistic (Fig. 5.2a-d) and cartographic (Figs. 5.3-5.4) elaborations for Pb and Acenaphthylene in the Gulfs of Naples and Salerno.



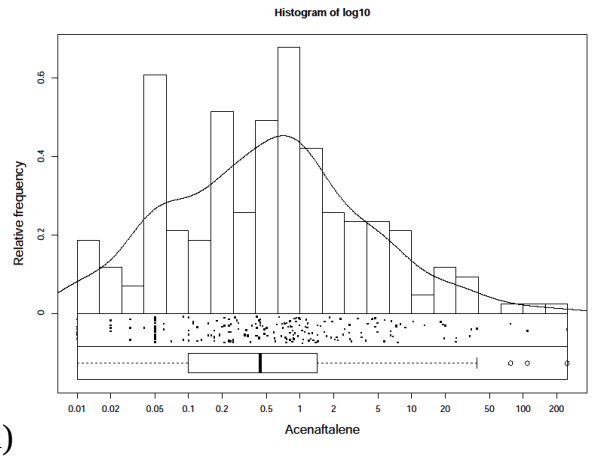
a)



b)



c)



d)

Fig. 5.2*: a) Example of CP plot in log scale for Pb, where the red line represents the threshold established by the law; b) Example of combination of histogram, box plot, scatterplot and the distribution function in log scale for Pb ; c) Example of CP plot in log scale for acenaphtylene; d) Example of combination of histogram, box plot, scatterplot and the distribution function in log scale for acenaphthylene.*

The dot and interpolated maps of Pb (Figs. 5.3-5.4)shows that the highest values (> 72 mg/kg, 70° percentile) are located exclusively around the Bagnoli site. The remaining concentrations , representing the 15 % of the data, is below the CSC threshold established by the Legislative Decree DM56/2009 (represented by the red line).

In the Acenaphthylene concentration distribution map, is it possible to observe that 95% of the samples have concentrations under 17 mg/kg. This 5% of high concentrations, reaching up 249 mg/kg, is located in three areas of the Gulf of Naples: in an extending out of Bagnoli in the Pozzuoli Gulf; in a wide area that goes from Marechiaro to Monte di Procida; offshore of the Sorrento Peninsula (NW of Punta Campanella).

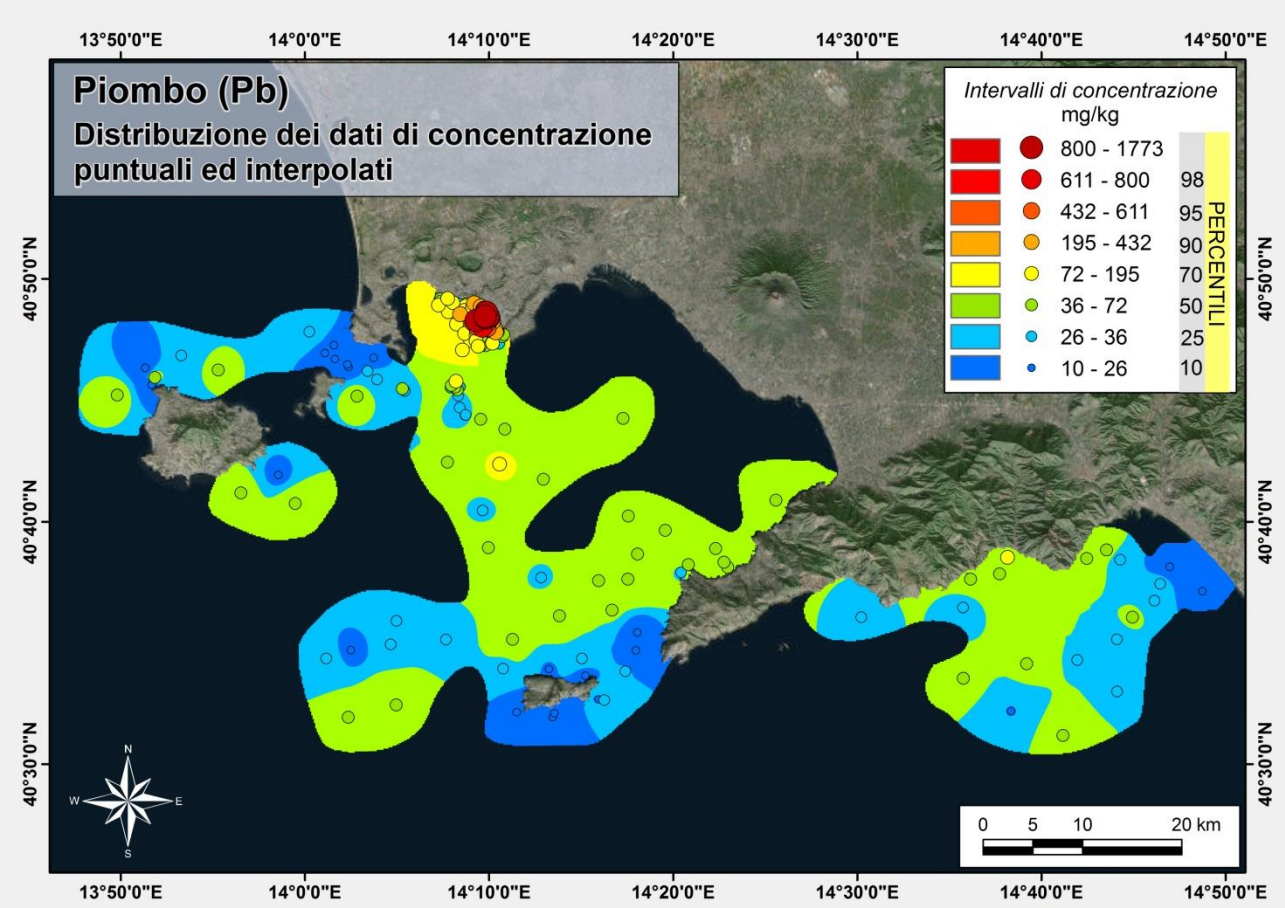


Fig. 5.3*: Example of dot map and interpolated map combination for Pb.*

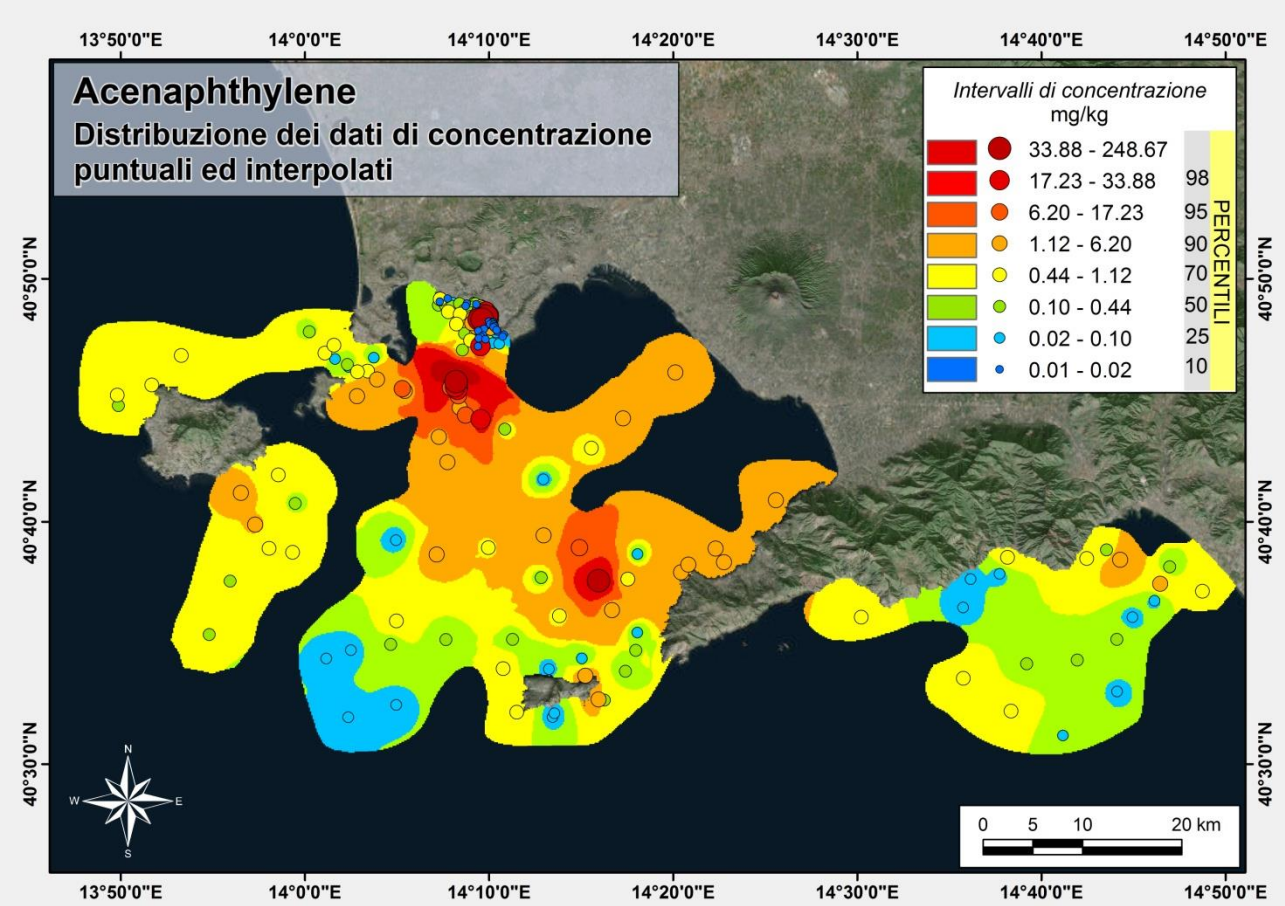


Fig. 5.4*: Example of dot map and interpolated map combination for acenaphthylene.*

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Here's to the ones who dream
Foolish as they may seem

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